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PROJECT: "USE OF COMPUTER MODELS FOR RISK ASSESSMENT
IN SOUTHERN FOREST ECOSYSTEMS"

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FINAL REPORT

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USE OF SIMULATION MODELS FOR ENVIRONMENTAL IMPACT ASSESSMENT OF FORESTRY HERBICIDES.

Increase herbicide usage in forestry applications such as site preparation and pine release, have generated a need for tools to assess the environmental fate of these herbicides in forested watersheds. However, models that have been developed for assessing pesticide movement have been designed to model agricultural settings. The hydrologic processes that dominate agricultural fields are not the same as the processes that dominate forested watersheds.

Two agriculturally based models are examined for their suitability in predicting pesticide movement in a forest setting: CREAMS (Chemical Runoff and Erosion from Agricultural Management Systems) from the USDA-ARS and PRZM (Pesticide Root Zone Model) from the US-EPA. Both models use a runoff curve number approximation to partition rainfall between overland flow (runoff) and infiltration. Neither model incorporates the turbulent subsurface flow paths or variable source areas important in forested watersheds. IBM PC-AT compatible versions of the agricultural field scale models CREAMS and PRZM were used to simulate pesticide movement from forested watersheds in the upper piedmont and the lower Appalachian mountains. Comparison of CREAMS simulations with measured hexazinone loss from a treated watershed in the upper piedmont showed that CREAMS accurately predicted hexazinone concentrations for storm events up to 75 days after application. For storm events occurring between 75 and 270 days after application, CREAMS underpredicted storm hexazinone concentrations. CREAMS predicted the following potential residue appearance in stormflow: bromacil > triclopyr > hexazinone > picloram > dicamba. Comparison of PRZM simulations with measured picloram movement in a forested southern Appalachian watershed showed that PRZM accurately predicted subsurface picloram movement when site modified runoff curve number, partition coefficient (Kd), and half-life (Ks) were employed.

Partition coefficient and pesticide half-life terms had the greatest impact on simulated pesticide leachability. With respect to Kd, PRZM predicts leaching from a forested mountain watershed as follows: Kd < 0.1, highly leachable; moderate potential leaching if hydrologic conditions are favorable 0.1 > Kd > 10, and Kd > 10 no leaching. A half-life of > 0.05 years is required for a compound to be persistent enough to leach below the root zone. The hydrologic components that affect water movement through the root zone also influence pesticide movement simulations.

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HERBICIDES IN SOUTHERN FORESTRY - IMPROVING WATER QUALITY. D.G. Neary, P.B. Bush, and J.L. Michael; USDA Forest Service, University of Florida, Gainesville, FL 32611; University of Georgia, Athens, GA 30602; and USDA Forest Service, Auburn, AL 36849.

ABSTRACT

Environmental interest groups have traditionally equated herbicide use with degradation of water quality. If the entire water quality picture is rationally analyzed, the conclusions are quite the contrary. Use of herbicides compared to mechanical site preparation improves or maintains water quality. Short-duration pulses of residues may appear in streamflow, but data from forest ecosystem studies indicates that these residues are generally not significant to aquatic ecosystems. The herbicides currently being used in southern forestry are low in toxicity and do not persist in the environment. Herbicide use significantly reduces the major, but frequently ignored, water quality problem, sediment. Site preparation with herbicides maintains watershed hydrologic conditions close to that of undisturbed stands and does not aggravate storm runoff, which can transport large amounts of sediment into streams. In addition, herbicide use does not produce adverse soil disturbance, which can lead to compaction and markedly increased soil erosion. Sediment displaced in streams produces significant and long-term changes in aquatic systems and can adversely affect stream biota and water quality large distances downstream.

INTRODUCTION

Passage of the Water Pollution Control Act of 1972 resulted in the focusing of considerable scientific effort on the sources and effects of nonpoint source pollution. Water pollution, any undesirable change in water quality, from nonpoint sources originates from a broad landscape rather than a single point. Types of nonpoint source pollution include sediment, nutrients, pesticides, toxic metals, livestock and sewage wastes, and atmospheric products. Of these, sediment comprises the greatest volume of pollutants and the single biggest problem (4). In-stream and off-stream damages from soil erosion and resulting sediment amount to $6 billion per year in the United States (5). Despite 14 years of research and implementation of best land management practices, nonpoint source pollution remains one of this nation's main water quality problems (20).

Forestry generally results in less nonpoint source pollution than agriculture due to a smaller land area, less intensive treatments, infrequent harvests and less frequent nutrient and pesticide applications. However, maintaining the quality of forest streams is a high priority since these waters have the best quality, are used frequently for municipal water supplies, support cold water fisheries, and provide recreational opportunities. Localized nonpoint source pollution problems can arise due to silvicultural activities, so most states have implemented best management

practices to protect the quality of forest lakes and streams (11). In all southern states silvicultural nonpoint source pollution is recognized as a localized problem affecting less than 50 percent of each state's waters. However, in North Carolina it is more of a widespread problem affecting over 50 percent of the water resources (1).

One of the best management practices that is being implemented more frequently in southern forestry is the use of herbicides for site preparation. For many years environmental interest groups have been arguing that use of herbicides in forest watersheds automatically equates to water quality degradation. However, when the whole nonpoint source pollution picture is analyzed objectively, the main water quality problem with silviculture is, like agriculture, sediment and soil erosion. The careful and professional use of herbicides in forestry can be a major factor in reducing nonpoint source pollution within forest watersheds.

The purpose of this paper is to briefly review the water quality implications of herbicide use in southern forestry. Water quality in its broadest sense of anion/cation chemistry, pesticide loading, aquatic habitat, and sediment loading will be considered. The question that ultimately will be addressed is, "Does herbicide use degrade, maintain, or improve water quality?"

WATER QUALITY - HERBICIDE RESIDUE CONTENT

Forestry herbicides can affect water quality at several phases in the use cycle. These phases consist of 1) transportation, 2) storage, 3) loading and mixing, 4) application, 5) equipment cleanup, and 6) container disposal. During application, the movement of residues into water is generally in the form of a diffuse nonpoint source. It is during application that most adverse public reactions and concerns for water quality arise. Thus, most of the environmental research in the past 10 years has focused on off-site movement during and after application. The other phases usually deal with concentrates, constitute potential point sources of pollution, and have historically caused the most problems for water quality.

During herbicide application in forest watersheds, movement of residues into surface or subsurface water occurs on a broad landscape scale. The main movement mechanisms are drift, leaching, and surface stormflow. Drift can be controlled by selecting appropriate application equipment, use of granular formulations, utilizing adequate buffer strips along streams, adding anti-drift adjuvants into spray mixes, and avoiding windy conditions or inversions. Leaching can be minimized by selecting the appropriate herbicide for individual soils and hydrologic conditions. Off-site movement in stormflow can likewise be minimized by careful application techniques.

The fate and movement of herbicides in forest ecosystems are governed by a complex interaction of physical, chemical, biological, and hydrologic processes. These include herbicide characteristics, climatic and hydrologic conditions, soil and microbiological processes, vegetation response, and application parameters. Some of the important application conditions include frequency of use, rate, application system, and timing. Rainfall, temperature, sunlight, and evapotranspiration are key climatic processes in

determining herbicide residue and fate. Herbicide chemical-physical characteristics such as solubility, volatility, and photodegradability are also important in determining residue fate.

Soil characteristics such as infiltration capacity, organic matter content, microbiological activity, structure, and texture mediate transport within and off-site. Vegetation uptake, degradation, and recycling of herbicide residues can also be key processes in determining herbicide fate. In a given situation, herbicides with the highest water solubilities, most resistance to physical, chemical, and biological degradation, lowest affinities for adsorption onto organic matter, and the highest application rates have the greatest potential for movement in the environment (16). The potential exists for herbicide residues to enter surface or subsurface water. The important questions are, "At what concentration, for how long, and of what importance?"

There are a number of studies on the fates of forestry herbicides in southern forests, but it is beyond the scope of this paper to address all of these. Several studies on hexazinone will be used to illustrate the range of water quality effects associated with herbicide application in southern forest watersheds.

Hexazinone residues in streamflow have been studied under operational-use conditions in several southern forest watersheds. Miller and Bace (10) reported high hexazinone concentrations (up to 2,400 ppb) from direct fall of pellets into a perennial forest stream. The hexazinone pellets were dropped when a helicopter overflew a streamside buffer zone. Concentrations fell to 110 ppb within 24 hours and to <20 ppb after 10 days. Concentrations of 1,000 ppb are needed to impact the most sensitive aquatic plants, and levels of 370,000 ppb are needed to have toxic effects on fish species such as bluegill sunfish. In another aerial application in Tennessee, hexazinone pellets were applied to 18 percent of a 440 ha (1056 ac) watershed at a rate of 1.7 kg/ha a.i. (1.5 lb/ac), but no streams were overflown (12). Hexazinone residues were never detected in streamflow during a 7-month period following the application.

In a more detailed study in the upper Piedmont of Georgia, four watersheds were treated with hexazinone at a rate of 1.7 kg/ha (1.5 lb/ac) (14). For the next year, 26 storms were sampled to determine hexazinone and metabolite concentrations in surface storm runoff. Residues peaked in the first storm after application (442 ppb) and declined with subsequent storms. Loss of hexazinone in stormflow averaged 0.53 percent of the applied herbicide, with two storms accounting for 59 percent of the chemical lost in runoff. Subsurface movement of hexazinone was detected 3-4 months after application in stream baseflow (concentration <24 ppb), but was short in duration (<30 days). Hexazinone residues were never high enough to adversely impact sensitive aquatic organisms (9).

Hexazinone was applied to a forest watershed in Arkansas to determine mobility and persistence of residues (3). The application rate was slightly higher than the Georgia study (2.0 kg/ha or 1.8 lb/ac), and the herbicide was not applied to intermittent stream channels. Consequently, the maximum hexazinone concentration did not exceed 14 ppb. However, low level residues

presisted in streamflow for a year after application. The amount of herbicide transported out of the watershed amounted to 2 to 3 percent of the applied chemical.

A study, currently in progress, is investigating hexazinone movement in watersheds treated by injecting trees with the liquid formulation. Monitoring of streamflow after operational applications in Alabama, Georgia, Tennessee, and Kentucky has not detected any hexazinone residues in streamflow.

From the studies mentioned above, it can be seen that residues detected in streamflow are generally low and short-term in nature. Since herbicide applications occur only once or twice in a stand's rotation, residue loadings on forest watersheds are small. Less than 3 percent of large forest watersheds would be treated in any one year, so in-stream dilutions are large. Thus, the water quality impact of forestry herbicide residues is minimal to none at all.

WATER QUALITY - NUTRIENTS

Any disturbance to forest ecosystems usually results in short-term increases in nutrient losses. These disturbances include logging, burning, site preparation, herbicide application, and insect and disease outbreaks. Data on this aspect of water quality in southern forests is limited as far as herbicide treatments is concerned. In a study reported by Neary et al. (15), application of hexazinone for site preparation produced short-term nitrate nitrogen increases that exceeded those measured for other forest disturbances in the South (7, 8, 18, 19). However, the peak concentration never exceeded the water quality standard and persisted for only 2 years.

Other anion and cation concentrations were elevated but were within the range of variations for forested watersheds in the region (15). The duration of the water quality response was small and short due to minimal soil disturbance and herbaceous plant recovery the second year after herbicide appliation.

Again, the downstream impacts of the increased nutrient outputs measured after herbicide application were small and not significant. This was due to the small magnitude of the measured increases and due to large dilutions from surrounding untreated watersheds. Thus, water quality was not adversely affected.

WATER QUALITY - SEDIMENT

It was stated earlier in this paper that sediment was the main nonpoint source pollutant in the United States. This holds for forestry land uses as well as other types. Once sediment is displaced off-site and into streams it becomes a long-term problem and can have considerable downstream impact. Herbicide residues transported into streams can still be degraded, but sediment remains in the stream and near channel alluvial areas. It is in this aspect of water quality that herbicides can improve water quality by reducing sedimentation of forest streams. In erosion sensitive areas, use of herbicides should be considered as a best management practice.

Mechanical site preparation has been utilized in southern forestry to improve regeneration success. The purposes of site preparation have been to 1) prepare the site for planting, 2) control weeds, and 3) improve microsite. The first has become less important in recent years with clean harvesting. The second, weed control, can be done more efficiently at a lower cost and with considerably less environmental impact by using modern herbicides.

Undisturbed forest watersheds normally have annual sediment yields of 3 to 700 kg/ha (3 to 640 lb/ac), depending on soils and physiographic region (Table 1). Herbicide application in the Piedmont increased sediment yield by 254 percent mainly as a result of increased water yield (15). Suspended sediment concentrations were only slightly elevated above undisturbed conditions, and bedload sediment was minimal. Mechanical site preparation in the Piedmont has produced very large (3,500 to 14,250 kg/ha) and significant first year increases in sediment loss (6). These losses approach agricultural levels and are often on soils less tolerant of sediment loss. Many forests in the South were established on eroded and abandoned agricultural land. These soils have begun to recover from past abuse, so good forestry would argue for management practices that protect the soil resource as well as water quality. Using herbicides for site preparation can eliminate the large sediment losses indicated in Table 1.

Another aspect of water quality that sediment can affect is the quality of aquatic habitat. Sediment displaced into forest streams can seriously affect habitat, spawning areas, and food sources as well as directly damage fish and invertebrates. Stream reaches choked with sediment have inherently lower species diversity and abundance (9).

CONCLUSIONS

Water quality can be adversely affected by inputs of sediment, nutrients, pesticides, toxic metals, livestock and sewage wastes, and atmospheric products. This paper has briefly examined the effects of herbicide use in forestry on water quality. Through examination of the whole water quality picture, it has been found that herbicide use can improve water quality by reducing the major nonpoint source water pollution problem, sediment. Problems can occur locally with herbicide residues in streams or lakes; but careful, well planned applications can eliminate any adverse effect on water quality. The positive water quality aspects of herbicide use in southern forestry have often been overlooked by the public, so foresters need to make more efforts to ensure that the real story on herbicides is told.

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Table 1. Sediment and water yields from site prepared forest watersheds in the South.

Reference	Treatment	Sediment Loss		Water Yield		Physio-graphic[1] Province
		Mass	% of Control	Area-Depth	% of Control	
		(kg/ha)		(cm)		
Neary et al. 1986	Control	67	--	3.4	--	P
	Herbicide	170	254	9.2	271	
Douglass and Van Lear, 1983	Control	39	--	15.5	--	P
	Burned	44	113	19.4	125	
Douglass and Goodwin, 1980	Control	35	--	4.0	---	P
	Kg, disk, grass	720	2057	8.7	218	
	KG	3501	10000	11.1	278	
	KG, disk	9730	28700	38.5	963	
Beasley, 1979	Control	620	---	2.9	---	UCP
	Chop	12540	2023	50.8	1752	
	Shea:	12800	2065	45.1	1555	
	Bed	14250	2298	50.7	1748	
Riekerk, 1982	Control	3	--	7.6	--	LCP
Neary et al., 1982	Burn,bed	7	233	12.9	170	
	window, bed	36	1200	21.4	282	

[1] P = Piedmont; UCP - Upper Coastal Plain; LCP = Lower Coastal Plain

PHYSICAL FACTORS IN FOREST HYDROLOGY

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ABSTRACT

There are many pathways that water can follow on its way
from the atmosphere to the stream in a forested watershed.
When only estimates of flow are required, it is not critical
that the actual flow paths are correctly identified. However,
because of the interdependence of water movement and chemis-
try, it is essential that the various flow paths and mechan-
isms of flow be correctly identified if stream chemistry or
contamination potential is to be understood. These flow paths
include immediate yield from saturated source areas (including
the wetted channel area), subsurface saturated and unsaturated
laminar flow, and subsurface turbulent flow. For an actual
watershed, this picture is confounded by topography, hetero-
geneity and anisotropy of flow factors, and fingering. These
factors will have a direct effect on the consequences of
atmospheric deposition of pollutants, nutrient cycling, and
the movement of chemicals applied to a watershed.

INTRODUCTION

When asked to describe or predict water quality, we usual-
ly begin by choosing some point in the channel downstream from
our point of interest. We then go to that spot, collect water
for chemical analysis, and if we are feeling sophisticated, we
even measure the streamflow. Armed with a few numbers, we
believe we can explain or predict what is happening on a
watershed scale. How naive we are! The values we measure are
a combination of what happens to the water chemically before
and after it gets to the stream. In this paper, we will
examine how water gets to the stream, how these pathways can
alter it chemically, and some of the confounding factors that
make these phenomena difficult to predict. We will then
examine these flow paths from a different perspective, and see
how the chemistry questions have often caused us to lose sight
of relevant hydrologic processes. This paper is an attempt to
tie together the various physical factors that affect flow on

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a watershed scale, and integrate them with the processes commonly examined on a microscale. By understanding the basic physical concepts, we hope this introduction will provide the framework necessary to understand the presentations that follow.

MAJOR FLOW PATHS

There are many pathways that water can follow in a forested watershed to reach a stream. The pathways followed, and the length of time spent by the water before reaching the stream, profoundly affects the water quality. Therefore, in order to understand water quality in a stream draining a forested watershed, or in an aquifer underlying a forested watershed, it is essential to understand the physics of flow in the watershed.

The original concept of flow from a watershed involved the deceptively simple concept of partitioning a hydrograph between baseflow and stormflow. A hydrograph is a graph of discharge plotted versus time for a particular location. The baseflow was thought to be saturated groundwater flow that resulted from deep percolation of some of the precipitation. This was viewed as a slow process, with the saturated water equilibrating chemically with the porous matrix through which it flowed. This water was considered to be the source of recharge for the underlying aquifer. Stormflow was thought to be overland flow, that is, water that did not infiltrate during a rain storm but ran off over the ground surface. Stormflow calculations based upon this concept could be made to yield reasonable estimates of peak flow or total flow from a forested watershed and they have been widely used. From a chemical point of view, however, they suffer from a fatal flaw: they are wrong. Rarely in upland areas of a forested watershed is the infiltration capacity exceeded by rainfall intensity. Thus, the pathway for flow assumed by this approach is appropriate for only a limited area of the watershed or for extremely disturbed watersheds where infiltration capacity has been reduced by poor management practices.

For a forested watershed, a better conceptual model for rainfall-runoff processes is the variable source area concept (Hewlett and Nutter, 1970). This concept defines a source area as a region, usually adjacent to a stream channel network, where near saturation or saturation occurs during the course of a storm by direct infiltration and lateral subsurface flow. As water is fed to the channel network the intermittent and ephemeral channels become active and move water quickly through and out the basin. This results in stream water containing a mix of unknown proportions of two kinds of water: water similar to atmospheric precipitation that fell directly on saturated areas and chemically modified subsurface flow. The size of the source areas are dependent upon the antecedent moisture conditions and the distribution of the rainfall (Dunne and Black, 1970; Dunne et al., 1975; Nutter,

1973). Upland areas, those areas beyond the source areas, will contribute flow by unsaturated, or possibly locally saturated subsurface flow. Such laminar flow is slow, and water that appears in a stream during the course of a storm by this mechanism may have been in the watershed for a considerable period of time. Hewlett and Hibbert (1963) demonstrated the ability of this mechanism to produce baseflow, even for long interstorm periods.

The soil of a forested watershed contains void spaces with a wide range of sizes. The small capillary size pores produce the unsaturated laminar flow previously described. There are a large number of pores, however, that are larger than capillary where water movement is by turbulent flow. They can be formed by soil fauna, living or dead plant roots, cracks and fissures, or subsurface erosion (Bevin and Germann, 1982). Under some conditions, these channels (called macropores) can provide a high speed conduit for the water, much like a drainage pipe. While in the macropores, the water may not come in contact with the soil roots or be chemically modified by interaction with soil particles as it travels to the stream. Consequently, macropores can provide a mechanism for rapid chemical movement with little chemical modification that produces water in streams that is quite different from water produced by subsurface flow mechanisms. However, these channels cannot actively transmit water unless the soil is saturated or the channel is connected with ponded surface water. If the soil is less than saturated, soil water cannot enter the large macropores and they act to retard movement of water, rather than enhance its movement. When a macropore is actively transmitting water, however, chemical diffusion into or out of the macropore may occur, depending upon the chemical gradient.   If the concentration of some ion is greater in the macropore than in the adjacent capillary pores, diffusion will occur into the capillary pores. If the concentration is greater in the capillary pores, the direction of diffusion will be reversed.

WATERSHED SCALE

Broadly speaking, we have defined three major flow pathways in a watershed: overland flow (almost always in a source area adjacent to a stream), subsurface saturated and unsaturated laminar flow, and subsurface turbulent flow in macropores. On a watershed scale, the occurrence and relative importance of these flow paths is not this simple; water does not choose one of these pathways and stay in it. Instead, an individual water molecule may follow several of these pathways on its way to a stream. This occurs as the result of a variety of watershed factors, including topographic shape, heterogeneity and anisotropy (spatial and directional differences) of soil flow properties, and moisture content differences that cause phenomena such as fingering, rapid spikes of water that move down ahead of the general front. We will examine each of these factors to assess their relative affect

on water movement, and therefore water quality.

On a first order watershed, the base of small valleys where intermittent streams flow form what are called zones of convergence. Subsurface flow is concentrated in these areas and the moisture content rises. As the storm progresses, they become saturated next to the intermittent stream channel and the stream begins to flow. Due to microtopographic relief, these zones may not be continuous down the slope, and the surface water may re-infiltrate. While they are active, these zones behave as source areas, with direct precipitation reaching the surface flowing system very rapidly with little chemical change. When the zones are not saturated, water infiltrates and begins to equilibrate with the soil. The length of time the water remains in the soil depends entirely upon the rainfall distribution and antecedent moisture conditions.

Uniform slopes, which do not concentrate water, and ridges, which cause the subsurface flow to diverge, are called non-convergent zones. They supply subsurface flow to the source areas, either adjacent to the channel or in the convergent zones. Except for very rare instances of extremely heavy rainfall, these zones produce no overland flow. Therefore, water moving from these areas will have an opportunity to chemically equilibrate with the soil.

Saturated and unsaturated laminar subsurface flow move by Darcy's Law. This law states that flow is equal to the hydraulic (energy) gradient times a factor called hydraulic conductivity. Conductivity is a function of the soil matrix properties such as pore size distribution, porosity, tortuosity, and properties of the fluid. For unsaturated conditions, hydraulic conductivity also depends upon soil moisture content.

Conductivity is highly variable in soils and can vary over several orders of magnitude in a few feet. When the hydraulic conductivity varies in space, the soil is called heterogeneous. Changes in hydraulic conductivity can markedly affect where and when water will flow. A common example of this phenomenon is a hardpan layer, where a clay layer retards the downward movement of water and causes the water to "pile up" above the layer. Because the clay has a much lower conductivity than the overlying soil, it takes much longer for water to move through it. Layers of lower conductivity, then, can cause saturated zones to form in areas where they are not normally found.

A coarse textured soil beneath a fine textured soil will also retard the water movement, although not for as long. Once the soil becomes saturated at the top of the coarse textured soil, the necessary additional energy will be available and water will move quickly through the non-capillary pores of the coarse textured layer. If the coarse textured

soil has some water in it before the start of the rain, the movement of water into the zone will occur in discrete columns, called fingers. If the coarse layer extends to the watertable (the top of the saturated zone), a large portion of the water may be moved through a relatively small volume of the soil. Therefore, chemicals traveling with the water may not have sufficient contact with soil particles to modify the pore water chemistry.

In most soils, the water can move more easily horizontally than vertically. This is due to a wide variety of geologic and soil forming processes. Thus, the hydraulic conductivity in the horizontal direction is greater than the conductivity in the vertical direction, a property called anisotropy. In layered sands the horizontal conductivity is typically twenty times greater than the vertical conductivity. In some cases, the horizontal conductivity can be a thousand times greater than the vertical conductivity. The practical result of this anisotropy phenomenon is to concentrate the water in the upper portion of the soil as it flows down slope, causing these watersheds to have more active and larger source areas.

SUBWATERSHED SCALE

The discussion thus far has concerned runoff processes on a watershed scale. This is the appropriate scale for understanding the relation between the watershed and stream water chemistry. Unfortunately, this scale is not easy to study. Most field experiments or physically based mathematical models have been smaller scale and have considered a hillslope or a plot. Physically-based hillslope models have generally assumed a two-dimensional vertical slice of the hill with water obeying Darcy's Law under saturated or unsaturated conditions (Freeze, 1978). These models cannot account for macropore flow, zones of convergence, fingering, or three-dimensional heterogeneity or anisotropy. It is possible for them to incorporate two-dimensional spatial heterogeneity and anisotropy, but this is rarely done because of lack of information concerning the distribution of conductivity in a real watershed. Three-dimensional models have generally assumed uniform conditions (Freeze, 1971). These types of models usually do not accurately predict a storm hydrograph.

Macropore flow has been modeled on a hillslope scale using a kinematic wave approximation (Bevin, 1981; Bevin, 1982; Sloan and Moore, 1984). This approach is conceptually similar to the approach used to estimate overland flow, with an empirically derived parameter. These models often predict a storm hydrograph more accurately than the saturated/unsaturated flow models, but because they are empirical they are not as useful for predicting chemical changes.

Tracers have been used to observe actual flow processes on a hillslope scale. Pilgrim et al. (1978), for example, used a radioactive tracer on a hillslope chosen for its uniformity.

The flow, however, was found to be very irregular. The irregular flow pattern was attributed to heterogeneous flow properties and the presence of macropores.

Most detailed observations of flow in a watershed are performed on a small plot. Usually it is assumed that the water flows vertically down as long as the soil remains unsaturated. The affects of macropores are generally ignored and all flow is assumed to occur as unsaturated laminar flow. This approximation reasonably describes zones of non-convergence, but is not very applicable for the source areas. Most stormflow from moderate storms, however, comes from the source areas adjacent to the stream or associated with zones of convergence (Liu, 1985). Because this water is an unknown mix of the unsaturated and saturated subsurface flow into the source area and runoff from direct precipitation on the source area, plot studies can only contribute to an understanding of a portion of the flow.

WATER QUALITY EXAMPLES

Water quality in a stream draining a forested watershed is dependent upon the flow paths followed, the residence time in those flow paths, and the source of the chemical constituents. This point will be illustrated by examining several water quality questions: acid deposition, nutrient cycling, and movement of chemicals applied to a watershed.

Chemicals in the atmosphere are loaded to the watershed by dry deposition between rainfall events and by precipitation during a storm. The concentration of chemical constituents is not constant over time; usually the highest concentrations occur during the early portion of the storm. During this early period, the source areas are not well developed and most of the water carrying the atmospheric contaminants infiltrates. Once infiltrated, the chemicals will often interact with the soil particles, limiting the distance that the pollutants can travel. Rainfall that lands on the source area will undergo little reaction and reaches the stream essentially unchanged. As the storm progresses, the source areas (especially in the convergent zones) expand, and a greater portion of the runoff reaches the stream with little chance to interact with the soil. However, by this time much of the atmospheric pollutant burden has been washed out. Thus, while a greater portion of the rainfall reaches the stream unmodified, the concentrations of pollutants are lower.

The fraction of the precipitation that enters the unsaturated zone is available to plant roots, along with the chemicals carried by the water. This occurs naturally for elements that are plant nutrients, and is called nutrient cycling. For some watersheds, nutrients are scarce and few are lost in stream discharge. Where there is an abundance of nutrients, more are often transported in the unsaturated/saturated flow system. If the nutrients enter the macropore system they can

be carried below the root zone or into the stream before they can diffuse into pore sizes that are available to roots, even if the system is nutrient poor. Measuring concentrations of nutrients in a stream will not allow one to determine the flow path followed by the nutrient on its way to the stream. Therefore this approach has little value in assessing nutrient dynamics on a watershed scale.

Wastes, fertilizers, and herbicides are often applied to forested watersheds and their fate depends upon the chemical characteristics of the particular chemical and the flow paths followed. In general, chemicals applied on or near a source area when the source area is active are likely to quickly appear in the stream. Chemicals applied to upland non-convergent zones, however, will be carried by infiltrating water into the unsaturated zone. The chemicals will then move slowly with the water, interacting with the soil particles. Chemicals that adsorb on soil surfaces are thus retarded in their movement.

These examples illustrate some of the reasons for the tremendous variability in water chemistry measured in a stream over time. Variability in chemical source strengths, the relative abundance of the various flow paths, and the relative contributions of these flow paths combine to produce many results.

SUMMARY

To understand the water quality of streams draining forested watersheds it is essential to understand the relative importance of the various pathways the water follows on its way to the stream. Water that infiltrates and flows in the saturated or unsaturated flow system will spend a relatively long time in the watershed and the water chemistry will be largely controlled by the soil through which it flows. Water that falls on active source areas or enters active macropores will reach the stream quickly with relatively little change of water chemistry. This water will look similar chemically to precipitation, or it may have a chemical constituent at significant concentrations that it acquired at the soil surface.

With respect to understanding stream water chemistry, we need to understand the flow paths of water on a watershed scale. For the most part, this is presently quantitatively not possible. Hillslope or plot scale models or experiments are usually used to estimate flow paths. While these approximations have their uses in deducing flow and chemical processes, care must be taken in extrapolating results from these studies to a watershed scale.

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ABIOTIC AND BIOTIC FACTORS AFFECTING FLOW

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For the estimation of flow from a forested watershed, evaluation of the relative importance of actual flow paths is not important.   Under-standing and prediction of chemical movement in nutrient cycling, however, requires a detailed understanding of the various flow paths on a watershed scale.

In general, the flow paths may be subdivided into three categories: surface flow, subsurface laminar flow, and subsurface turbulent flow. Surface flow can include classic Hortonian overland flow, immediate flow from saturated zones adjacent to stream channels, and direct precipitation on the wetted channel area.   Subsurface laminar flow is all saturated and unsaturated flow obeying Darcy's Law.   Subsurface turbulent flow includes all subsurface flow that does not obey Darcy's Law.   This flow is often called macropore flow.   Water in a first-order stream reflects the mixing of waters from these general flow paths in unknown and complicated combinations.

A number of site specific factors, as well as factors associated with site disturbance, can affect actual flow paths.   The flow paths followed will change in space and time reflecting changed watershed conditions. Furthermore, the factors can differentially affect the flow processes and can cause a shift in the relative importance of a flow path.

Site specific factors can be subdivided into abiotic and biotic factors. Abiotic factors include spatial heterogeneity of flow properties, anisotropy of flow properties, slope morphology, and surface morphology. These factors principally affect subsurface laminar flow.   Biotic factors include above ground vegetative affects (stem flow, throughfall, and litter layer formation), and below ground vegetative affects (principally root activity).

Activities that disturb a watershed may cause a shift in the relative importance of various flow paths.   Abiotic factors such as windthrow, soil

piping, karst processes, landslides, and soil creep can cause flow change. Biotic factors such as burrowing organisms (from gophers to leafcutter ants) and root decay primarily affect subsurface turbulent and subsurface laminar flow.

Harvesting a watershed can produce a number of changes to flow paths. Macropore formation may be greater in an area that is periodically disturbed, especially as larger roots decay. This may result in a reduction of nutrient loss, as large quantities of water bypass the unsaturated zone. The rapid shunting of water may be especially important in tropical areas, where many soils are nutrient poor and leaching rates can be high.

The influence of site disturbance on flow paths are illustrated using data from a study done in the Florencia Norte Forest, near Turrialba, Costa Rica. The area is Tropical Premontane Wet Forest with a mean annual rainfall of approximately 2700 mm. The soils are Typic Dystrandepts developed from aged-volcanic bedrock and recent-pyroclastic materials. The physical structure of the soil is good, stabilized by the large amount of organic matter in the upper soil horizons and allophane throughout the profile. The soil is strongly aggregated, has a high infiltration rate (approximately 35 cm h^{-1}), and has a very high water-holding capacity (at tensions of 15 bars the volumetric moisture content was 30%).

Total rainfall for 1979 was 198 cm and for 1980 was 244 cm. The 1979 rainfall was substantially less than 34 year average of 266 cm recorded at the nearby CATIE weather station. A network of zero-tension lysimeters were used to collect soil water from a site composed of undisturbed natural succession and a site composed of periodically disturbed agricultural vegetation. Soil solutions collected were analyzed for NO_3-N, K, Ca, and Mg. Shallow lysimeters in the disturbed site consistently collected greater flows than in the natural site. Deep lysimeters were more consistent between sites in collection volume. The increased volume is attributed to increased macropore flow and decreased unsaturated laminar flow following disturbance. This results in less leaching of nitrogen from the disturbed sites. Fluxes for potassium, calcium and magnesium were not significantly affected.

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ABSTRACT

The agricultural field scale models CREAMS (Chemical Runoff and Erosion
from Agricultural Management Systems) and PRZM (Pesticide Root Zone Model)
were used to simulate pesticide movement from forested watersheds in the upper
piedmont and the lower Appalachian mountains.   Comparison of CREAMS simula-
tions with measured hexazinone loss from a treated watershed in the upper
piedmont showed that CREAMS accurately predicted hexazinone concentrations for
storm events up to 75 days after application. For storm events occurring
between 75 and 270 days after application, CREAMS underpredicted storm hexazi-
none concentrations. CREAMS predicted the following potential residue appear-
ance in stormflow: bromacil > triclopyr > hexazinone > picloram > dicamba.
Comparison of PRZM simulations with measured picloram movement in a treated
forested southern Appalachian watershed showed that PRZM accurately predicted
subsurface picloram movement when site modified runoff curve number, partition
coefficient (Kd), and half-life (Ks) were employed.

Partition coefficient, pesticide half-life, and water infiltration terms
had the greatest impact on pesticide leachability. With respect to Kd, PRZM
predicts leaching from a forested mountain watershed as follows: high
leaching for Kd < 0.1, potential leaching if hydrologic conditions are favor-
able for 0.1 > Kd > 10, and no leaching for Kd > 10.   A half-life of > 0.05
years is required for a compound to be persistent enough to leach.

INTRODUCTION

An ever increasing population is resulting in an increased demand for
food, fiber and timber production on decreasing acreage.   This increasing
population and industrial growth is also taxing water resources and limiting
present and future development.   In attempts to maximize forest productivity
in a cost effective manner and minimize the detrimental impact of forest
practices on water quality, the forest industry is increasing its use of
herbicides in site conversion, site preparation and pine release.

The US-EPA regulates the registration and use of all pesticides. In order
to register a herbicide for forest use under Vol. 40 CRF, #158, the registrant
must conduct a risk assessment that involves:

1. Collection of site specific residue dissipation data including: foliar
    washoff, foliar and soil dissipation, offsite movement, aquatic impact
    and bioaccumulation, and offsite transport.

2. Utilizing available environmental models such as CREAMS and PRZM,
    describe the fate of the chemical at other locations with different
    site characteristics and climatic conditions.

In order to understand pesticide behavior in a forested watershed, we need first to understand water movement as it is the vector for pesticide movement. There are three major flow paths for water movement in a forested watershed: 1) overland flow, which rarely occurs in a forested watershed, 2) subsurface saturated and unsaturated laminar flow (Darcian flow), and 3) subsurface turbulent flow in macropores.

In attempting to model pesticide movement in a forested watershed we have a problem with scale. On a watershed scale, processes such a variable source area, convergence and divergence of flow, lateral diffusion, and channeling make modeling attempts difficult. If we attempt to predict pesticide concentrations in a stream, and the application is in the upland portion of the watershed, the conventional methodologies for predicting pesticide concentrations in the stream do not work. That is, we can not rigorously model the physical process. We can make some guesses on a plot scale but we can not predict weir concentration.

Most of the time we treat pesticide movement as a plot scale problem: water-born pesticide moves with the unsaturated flow in one dimension (depth). By measuring lysimeter pesticide concentrations with time, we can attempt to examine the flow processes.

The fundamental equation most commonly used to predict pesticide movement beneath the soil surface is the advection-dispersion equation. It assumes that flow behaves according to Darcy's Law: flow equals hydraulic conductivity times hydraulic gradient, and thus flow is known. The major components of the advection-dispersion equation are:

Dispersion - the decrease of chemical concentration with distance because of mechanical mixing and molecular diffusion.

Advection - the movement of the front with the apparent velocity of the fluid.

Source/sinks - local losses or gains of the mass of pesticide by processes such as plant uptake, chemical decay, or hydrolysis.

Adsorption - adsorption on soil particles.

On a forested watershed, the movement of a pesticide is not this simple. Factors that would affect pesticide movement and may not be included in an advection-dispersion model are convergent/divergent flow zones caused by the topography of the watershed, spatial variability of flow and transport processes, directional components of flow and transport processes, and zones of preferred flow.

Environmental models developed for agricultural use that may be adaptable to a forest watershed situation include CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems) and PRZM (Pesticide Root Zone Model). The CREAMS model is a physically based, daily simulation model that estimates stormflow, sediment transport, and nutrient and pesticide movement from field-sized areas. Simulation of pesticide movement by CREAMS provides total mass and storm-mean concentrations on a field-edge basis and does not provide

information on downstream routing or subsurface fate. The Pesticide Root Zone Model (PRZM) is a dynamic, compartmental model for use in simulating chemical movement in the unsaturated soil systems within and below the plant root zone. Time-varying transport, including advection and dispersion are represented in the program.

The objectives of this study were to determine:

1. How accurately a non-site specific model, such as CREAMS and PRZM could predict chemical losses in storm flow from small forested watersheds.

2. If CREAMS predictions were adequate, determine how alternate herbicides rate in terms of runoff potential on the hexazinone study site.

3. If PRZM predictions were adequate, evaluate the leachability of alternate chemicals on the picloram study site.

METHODS AND MATERIALS

<u>Hexazinone</u> <u>Field</u> <u>Study</u> <u>For</u> <u>CREAMS</u> <u>Verification</u>. The hexazinone study site was located in the upper Piedmont of north Georgia within the drainage of Moonshine Creek, a tributary of the Broad River. A complete description of the study site is given by Neary <u>et</u> <u>al</u>. 1983. Briefly, the site consists of five sub-watersheds with well-defined ephemeral channels. The watersheds were wide and bowl-shaped in their upper reaches, incised at their midpoints, and broad-bottomed in their lower reaches. The channel area in the lower reaches contain fine-textured, alluvial deposits that occasionally reach 2m in depth. Soils on the ridges and slopes are sandy loam typic Hapludults of the Cecil series with an A horizon 0 to 10cm thick overlying a massive B2t horizon. The A horizon increases in thickness on the slope toe.

Five watersheds, 0.85 to 1.09 ha in size were instrumented in 1979 (Neary <u>et</u> <u>al</u>, 1983). Water samples were collected from 26 stormflow events from April 26, 1979, to May 27, 1980, and the hexazinone residue levels were determined (Neary <u>et</u> <u>al</u>. 1983). All flow occurred as stormflow, that is, at no time during the study period did baseflow occur.

<u>Picloram</u> <u>Field</u> <u>Study</u> <u>For</u> <u>PRZM</u> <u>Verification</u>. The upper slopes of Watershed 19 at the Coweeta Hydrologic Laboratory, Otto, North Carolina was divided into two 2 ha plots and hand treated with a 10 percent active pelleted picloram herbicide formulation (May 15, 1978) at a rate of 5.0kg ha-1 (Neary <u>et</u> <u>al</u>. 1986). Watershed 19 is a 28 ha watershed with a northern exposure. It ranges in elevation from 792 to 1112 m. Annual rainfall averages 2054mm , but can range from 1200 to 2500mm. Slope, which averages 27% from the weir to the top, is typically 35 to 40% on most side slopes, but often exceeds 100% in the upper elevations. The soils are mainly Saluda stony loams, coarse-loamy, mixed mesic Umbric Dystrochrepts derived from pre-Cambrian gneiss, metasandstone, schist, and quartzite. These soils have a fairly high organic matter content in the A horizon. Permeability throughout the profile is rapid with some reduction in the B horizon. The saprolite has weathered isovolumetrically (30% porosity) and thus does not act as a restrictive layer to drainage

(Velbel, 1985). Bedrock occurs at variable depths (2-5m).

The forest stand is a mixture of low-quality hardwoods dominated by chestnut oak (Quercus prinus L.), scarlet oak (Q. coccinea Muenchh.) black oak (Q. velutina Lam), and hickory (Carya spp.). Rhododendron and mountain laurel form an almost impenetrable understory thicket (> 18,000 stems ha-1) which, in some instances, prevents direct sunlight from reaching the forest floor (Neary et al., 1979).

The watershed was instrumented in 1978 (Neary et al., 1986). On each of the plots, four sets of porous cup tension lysimeters were installed 15m uphill from the lower plot boundary. Previous research has shown that porous ceramic cups do not adsorb appreciable amounts of picloram (Rao et al., 1974). Each set contained a 0.3-, 0.6-, and 1.2-m deep lysimeter sampling from the Bt1, Bt2, and C horizons, respectively. Rainfall data were obtained at the permanent climate station adjacent to the picloram treated watershed.

Soil solution was sampled with porous cup tension lysimeters (0.02 MPa tension) on a weekly basis (Hansen and Harris, 1975). Periods of drought and winter snowpack caused gaps in the sampling record.

Mineral soil samples were collected from the two picloram-treated plots after the first rainfall following herbicide application. Sampling continued until mid-December of 1978. A bucket auger was used to collect samples from a depth of 1.2m. Each separately analyzed sample consisted of ten composites. The auger was rinsed with distilled water between each sample to reduce cross contamination. The bottom and top portions of each bucket sample were also discarded to reduce sample contamination.

CREAMS Computer Simulation. The CREAMS model is composed of a series of submodels linked together to yield an integrated estimate of stormflow, percolation, erosion, and dissolved and absorbed plant nutrients and pesticides. The hydrology submodel drives the remaining submodels, and provides the transport medium for sediment and chemicals. Daily precipitation totals are required, and stormflow is predicted using the SCS runoff curve number method. Because there was a negligible sediment loss for the watershed over the 13-month sampling period (Neary et al., 1983), the erosion portion of the CREAMS model was by-passed. The average physical parameters for the site required by the hydrology submodel were taken from published sources (Holtan, et al., 1968; Neary, et al., 1983) or calculated according to instructions in the CREAMS manual (Knisel, 1980). Required input data to the hydrology submodel other than rainfall are mean monthly temperature and radiation, watershed physical parameters, and soil hydraulic properties.

The pesticide submodel of CREAMS allows specification of different decay rates for chemical residues on the soil. Movement of pesticide below the soil surface (one cm) was estimated for highly soluble compounds, but vertical and horizontal movement at greater depths over time are not simulated. Concentrations of herbicide in solution and adsorbed onto sediments, as well as the mass transported by each process are calculated. Pesticide residues remaining in the soil surface and total pesticide loss are totaled after each storm.

The most significant CREAMS input parameters for the pesticide submodel are given elsewhere (Nutter et al., 1984). Application rate and date deter-

mine the amount of herbicide exposed to storm runoff events, as this is a function of loading and rainfall frequency patterns. For pesticides with a water solubility greater than one ppm, CREAMS assumes that the availability of the chemical for vertical transport with infiltrating water is described by a pesticide distribution coefficient, Kd. This coefficient is defined as the ratio of pesticide concentration in the soil to the concentration in solution at equilibrium. The main assumptions regarding Kd are that it is independent of pesticide concentration and that adsorption/desorption processes in the soil are rapid, reversible processes. Kd is related to percent organic content and calculated specific surface of the soil (Pionke and DeAngelis, 1980). Another important pesticide parameter is the decay constant, Ks. Pesticide dissipation from the surface one cm of soil is described by a simple exponential function which combines photodegradation, volatilization, microbial breakdown, and other processes. The decay constant is then used in a first-order rate expression to compute surface concentrations over time.

To evaluate runoff potential and to assess the potential risk of maximum concentrations appearing in stormflow for five different herbicides (hexazinone, bromacil, triclopyr, picloram, and dicamba), CREAMS simulations were run for each herbicide using daily rainfall records for Cornelia, Georgia (Climatological Data, National Oceanographic and Atmospheric Administration, U.S. Department of Commerce) and the mean watershed characteristics. To generate sufficient frequency of stormflow events the hydrology and pesticide submodels were run for 50 years (1931-1980) with the specified herbicide application repeated on the same date (May 1) each year. In this way a probability of occurrence can be associated with the concentration of herbicide in stormflow following application.

The simulation results were tabulated and the probability of occurrence for various stormflow concentrations were calculated using standard hydrologic techniques. This approach was suggested by Wauchope (1978) to evaluate potential impacts of pesticide runoff to downstream aquatic systems. The maximum annual simulated concentration for each herbicide (i.e. the annual series) was selected and the probability of occurrence for each event calculated using the Weibull plotting position formula (Viessman et al. 1977).

PRZM Computer Simulations. PRZM is a dynamic compartmental model for use in simulating chemical movement in unsaturated soil systems within and below the plant root zone. Time-varying herbicide transport is represented in the program by a finite difference solution of the the advection/dispersion equation. For this study, the dispersion term was set to zero and transport was simulated by advection modified by decay and adsorption.

The PRZM simulations were conducted in three phases. First, a PRZM simulation was run using parameter values estimated using the PRZM manual (Carsel et al, 1984) and long-term meteorological data obtained from the Coweeta Hydrologic Laboratory. Second, hydrologic and pesticide dissipation parameters were adjusted to allow PRZM to more closely approximate the measured picloram data. Third, multiple PRZM simulations with site modified hydrologic values were conducted to determine the impact of Kd and Ks on potential pesticide leaching.

Initial PRZM model simulations were run using long-term daily rainfall, temperature, pan evaporation data obtained from Coweeta Hydrologic laboratory.

Watershed physical parameters, and soil hydraulic properties were taken from published sources or measured on site. Pesticide parameters for picloram were given or estimated using the PRZM manual or obtained from the National Research Council of Canada (1974). Because a pelleted application was being simulated, it was assumed that all herbicide was applied to the soil surface.

PRZM estimations of plant interception and evaporative losses yield approximately 10% rainfall interception loss. Evapotranspiration was estimated from pan evaporation data or from empirical formulas using average daily temperature (Pan factor=0.75). Predicted canopy evaporation and evapotranspiration values (Figure 3) are in reasonable agreement with values expected for a forested watershed.

The hydrology component for calculating runoff and erosion is based on the Soil Conservation Service runoff curve number technique and the universal soil loss equation. The erosion algorithm was included but was insignificant since overland flow and resulting erosion are not major components in forested watersheds. The runoff component is essentially zero for the default simulations.

For overland flow this is correct; very little overland flow occurs on a forested watershed. However, the relatively rapid hydrograph responses of watersheds at Coweeta Hydrological Laboratory suggest that rapid flow paths exist, such as macropore flow. Such a flow path would result in movement of the pesticide to the stream with little opportunity for adsorption or decay. As a result, the runoff component in modified simulations was set to predict approximately 10% annual total runoff by adjusting the runoff curve number from 55 to 75. By increasing the runoff component, the amount of water available for infiltration is decreased. Evapotransporation component changes less than 2-3% and results in minor predicted pesticide concentration changes.

The Kd values are dependent upon the organic matter in the soil and were calculated by the PRZM manual (Carsel et al. 1984) for the default simulation. The default half-life (Ks) was obtained from the PRZM manual. To determine the effect of Kd on pesticide leaching, the Ks was set at 0.0005 days-1 (half-life=five years), and the Kd was varied from 0.001 to 1000. Likewise, the effect of Ks on leaching was determined by setting the Kd to 0.1 and varying the Ks from 1 to 0.001 years-1.

The CREAMS program was used without modification to simulate conditions at the hexazinone study site using an IBM 3081 mainframe computer at the University of Georgia. PRZM simulations were run on an IBM-PC modified to be the equivalent of an IBM-AT.

RESULTS AND DISCUSSION

The results for the CREAMS simulation of the hexazinone application and its comparison with the field measurements are shown in Figure 1. As expected, the stormflow events with the highest hexazinone concentrations were those closest to the application date. The predicted concentrations decreased over time until 150 days after application, when only small amounts of hexazinone (< 0.01 ug/1) were predicted in stormflow. The predicted and measured

concentration were similar for the first 75 days. However, between 75 and 270 days the measured herbicide concentrations remained elevated at 10 to 20 ug/l. In the next stormflow event after 270 days (at 320 days), the herbicide concentration was not detectable.

Predicted and actual hexazinone concentrations in the stormflow are in close agreement for events occurring 0 to 75 days after application. For storms occurring more than 75 days after application, the model consistently underpredicts hexazinone concentrations in stormflow. The inability to predict hexazinone concentrations after 50 to 75 days may be due to a change in the source of the hexazinone to stormflow.

The source area for stormflow is the ephemeral stream channel and the immediate surrounding area. This is the only portion of the watershed where overland flow is likely to occur. The model predicts the declining hexazinone availability in the source area, but cannot include the addition from the delayed, up-slope subsurface flow. Because this version of CREAMS model does not account for movement of herbicide within the soil, it would not predict the continual supply of herbicide to the channel region.

CREAMS simulations run for a 50-year period of record using the daily rainfall hydrology submodel show that of the five herbicides tested, bromacil, hexazinone, and triclopyr have the greatest potential for movement in stormflow from the forested Piedmont watersheds (Figure 2). Bromacil concentrations declined the least as the recurrence interval decreased. This results from bromacil's tendency to bind to clay and organic matter colloids (high partitioning ratio, Kd=10), hence its long residuence time in the soil surface. The concentration of bromacil simulated in stormflow can be expected to be greater than 1000 ug/l at least once every 8 years (12 percent probability of occurence). In contrast, simulated concentrations of picloram and dicamba (Kd < 1) do not exceed 30 ug/l (Figure 2). Thus, bromacil and triclopyr, with high Kd values and moderate-to-low solubilities, and hexazinone with a high solubility and moderate Kd value produced greatest concentrations in runoff.

The low predicted storm runoff concentrations at Kd < 1 (picloram and dicamba) can be attributed to reduction surface concentrations of pesticide due to leaching prior to stormflow. Because the partitioning ratio reflects the tendency to absorb to clay and organic matter colloids, a low Kd means a pesticide has only a weak tendency to bind to colloids. Both herbicides have negative charges have only a weak tendency to bind to colloids in the acid soil. As a result, they leach out of the surface soil horizon. Before CREAMS calculates the pesticide available for extraction to stormflow, the amount of pesticide available is reduced by the vertical movement of pesticide out of the surface zone in the percolate. The amount removed in this way is mainly a function of Kd. Thus, herbicides with low partitioning ratios such as picloram (Kd = 0.7) and dicamba (Kd = 0.077), will not be available in the surface zone for extraction to stormflow.

PRZM hydrologic simulations employing long term hydrologic records accurately predict the hydrologic summary parameters such as rainfall interception loss and potential evapotranspiration (Figure 3). PRZM predictions of pesticide concentrations are not extremely sensitive to differences in evapotranspiration. The model is much more sensitive to parameters that directly affect pesticide availability: rate of application, partition coefficient

(Kd), and pesticide decay rate (Ks).

The summary of PRZM simulation outputs (Figure 4) show that the pesticide decay component accounts for most of the picloram loss. In both the default and modified simulations approximately 4.5 kg/ha out of the 5kg/ha applied are lost via decay. Picloram loss via plant uptake is approximately 0.25kg/ha. Slightly more uptake is observed in the modified run than the default simulation since a longer decay rate was used. The second year breakthrough is about the same for both the default and modified simulations. No breakthrough was predicted in the first year by either simulation. By forcing the 10% runoff in the modified simulation and conceptualizing this as macropore flow, the modified simulations predicts more pesticide movement via runoff than the default simulations (Figure 4). In either case, the erosion component is essentially zero.

The predicted picloram soil solution concentrations are compared with the PRZM simulations at 30, 60 and 120 cm in Figure 5. At 30cm the default and modified PRZM simulations overpredicted the measured picloram concentrations. The default and modified PRZM simulations accurately predicted the timing and duration of picloram movement through the 30 cm zone. Default PRZM simulations with Kd values of (0.175 - 0.007) predicted that the picloram would move through the 60 and 120cm soil depth more rapidly than observed. Increasing the Kd in the modified PRZM simulations retarded the simulated pulse of picloram movement through the 60 and 120 cm soil depths and produced better agreement with observed data.

Modifying the Ks from 0.019 to 0.005 improved the agreement between the PRZM concentration prediction and measured picloram levels. By increasing the half-life, the site specific simulations allowed more of the picloram to reach 60 - 120 cm levels prior to decay. Since the decay process is the major dissipation process for pesticide disappearance in the model (Figure 4), it is critical that the estimation of Ks be as accurate as possible. Use of half-life values obtained by measuring pesticide dissipation from the top 0-3" or 0-6" soil layers will underestimate the flux below the root zone. Use of hydrolysis or reduction rate constants below the mycorrhizal zones would give a better estimate of Ks.

The rizosphere in the top 25-30cm contains many large void spaces, channels for lateral dispersions, root channels, piping and worm holes which account for macropore flow. At depths below 30-60cm less biological activity and finer roots occur and as a result more uniform mixing occurs. As a result, a significant portion of the water passing through the surface zone does not follow Darcy's law. With depth the flow processes tend to be more Darcian and the model assumptions are more realistic.

Several significant pulses of picloram were detected in soil cores take shortly after the picloram application (Figure 6). These pulses occur much too quickly, contain much higher picloram levels and dissipate much more rapidly tnan Darcian flow would predict. These pulses are attributable to pathways other than Darcian flow, such as macropore flow and active root transport.

To determine the effect of Kd on potential pesticide leaching from the Coweeta forested watershed, the half-life was set to five years and the Kd was

varied from 0.001 to 1000. PRZM predicts that less than 10 kg/ha of chemicals with a Kd $\geq$ 10 (classical chlorinated hydrocarbon insecticides, synthetic pyretheroids and paraquat) will not leach below the root zone within two years of application (Figure 7). As much as two kg/ha may leach through the root zone when persistent chemicals with Kd values of $\leq$ 0.1 (phenoxy herbicides) are simulated. Compounds with Kd values of 0.1 - 10 (triazine, uracil, carbamate, and urea based herbicides) may show leaching below the root zone during wet years.

The affect of Ks on potential pesticide leaching was evaluated by setting the Kd value to 0.1 and varying the half-life from 1 day to 5 years (Figure 8). Compounds with a half-life of <0.05 years will not persist long enough to leach below the root zone. Compounds with a half-life >0.5 years have the potential to leach below the root zone if the Kd is <10. Compounds with a half-life between 0.05 and 0.5 years may leach if hydrologic conditions are favorable.

The Kd is highly dependent upon the organic carbon content and pH of the soil for organic acids. If highly mobile chemicals that produce an onsite Kd of 0.1 or less are to be used on the mountain site, attempts should be made to modify one or more of the factors that directly affect pesticide availability: rate of application, Kd, or Ks. For example, the application rate could be reduced by substituting using stem injection for spray application. In addition, the Kd and Ks may be altered by modification of the formulation.

CONCLUSIONS

In conclusion, comparisons of predicted hexazinone concentrations in stormflow from forested watersheds with field data demonstrate that CREAMS, an agricultural runoff model, can be used to predict the herbicide concentrations in stormflow occurring shortly after application. From the standpoint of environmental impact, maximum stormflow residue concentrations occur shortly after application and CREAMS estimated those concentrations within $\pm$ 15 percent. The current version of CREAMS does not account for subsurface movement and thus tends to underpredict concentrations that may be influenced by subsurface flow processes.

CREAMS is useful in evaluating alternative forest herbicides for their potential to appear in stormflow. The model predicts the following order of potential for appearance in stormflow: bromacil > triclopyr > hexazinone > picloram > dicamba. Highly soluble herbicides (picloram and dicamba) with low partitioning ratios (Kd) were not readily lost to stormflow. These compounds move down through the soil profile with infiltrating rainfall and are not available at the soil surface. Subsurface flow models and/or later versions of CREAMS currently under development will likely be more reliable in predicting the movement of picloram and dicamba.

The site-specific PRZM simulation reasonably predicts the movement of picloram through the soil profile at Watershed 19, Coweeta Hydrologic Laboratory. The shape and duration of the picloram movement accurately match the observed values and is conservative in its estimation of predicted pesticide

concentrations. Rapid movement of water through the watershed as macropore flow, a process not explicitly simulated in the model, may result in long distance pesticide movement and produce detectable pesticide levels in early runoff events (Neary et al. 1986). Macropore flow could also account for high concentrations of picloram observed in some lysimeters soon after application.

PRZM simulations are sensitive to the rate of pesticide application, Kd, Ks, and water available for infiltration. Mobile, persistent chemicals (Kd < 0.1, half-life > 0.5 years) may readily leach below the root zone. Immobile compounds (Kd > 10) or non-persistent compounds (half-life < 0.1 year) will not leach below the root zone. Compounds of intermediate mobility (0.1 < Kd < 10) may leach if sufficient infiltration occurs. PRZM also predicts that most pesticide leaching below the root zone occurs during the second year following application.

Attempts to take a non-site specific model and apply it to a new situation may or may not give a good prediction of what will happen. A model needs field data for validation and calibration. Field data needs modeling to help understand the processes involved and to direct proper sample collection.

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TABLE 1. Summary of book value (default) and modified (site specific) parameters used in PRZM simulations.

Parameter	Depth	Default	Modified
Runoff curve number		55	75
Kd	1	0.175 (cm3gm-1)	.20 (cm3gm-1)
	2	0.021	.20
	3	0.016	.20
	4	0.016	.20
	5	0.007	.20
Decay rate			
Ks	top	0.018 (days-1)	0.01 (days-1)
	below	0.018	0.005
	surface		

KEY WORDS: CREAMS, PRZM, field scale model; herbicide residue; forests;

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Ks	top	0.018 (days^{-1})	0.01 (days^{-1})
	below	0.018	0.005
	surface		

Figure 1. Mean Predicted and Actual Hexazinone Concentrations in Stormflow as a Function of Time After Application.
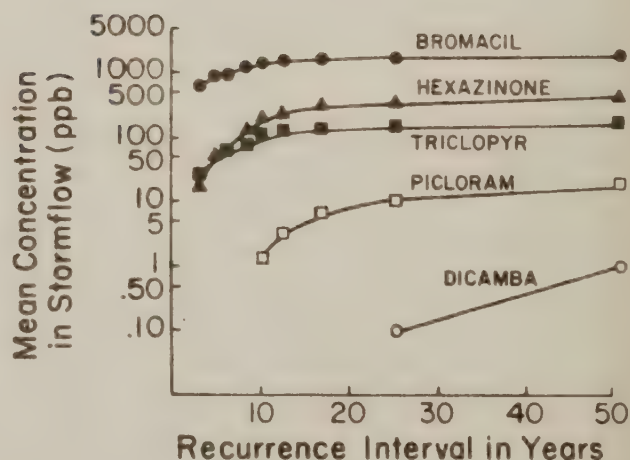
Figure 2. Reoccurrence Intervals of Maximum Annual Concentrations for Various Pelleted Herbicide Applications on May 1 Each Year as Predicted From 50 Years of Stormflow and Herbicide Concentration Simulations by CREAMS.

PRZM Hydrologic Summary

P □ CE ■ RO ▨ I ▨ ET

Default Values

Modified Values

Volume - cm

Year
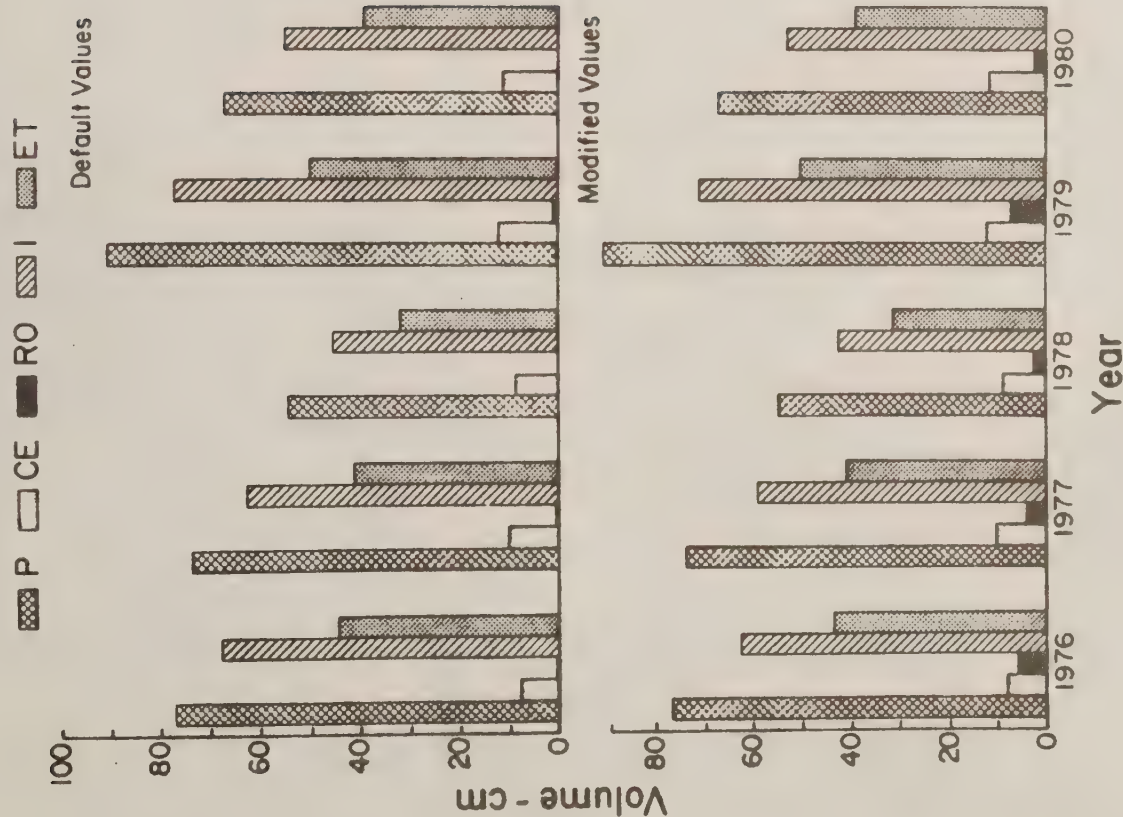
Figure 3. Hydrologic summary for PRZM simulations of Watershed 19, Coweeta Hydrologic Laboratory. (P=precip; CE=canopy evap; RO=runoff; I=infiltration; ET= evapotranspiration).

Pesticide Flux Summary

Two Simulations

Picloram Flux - kg/ha/yr

Simulation-Year
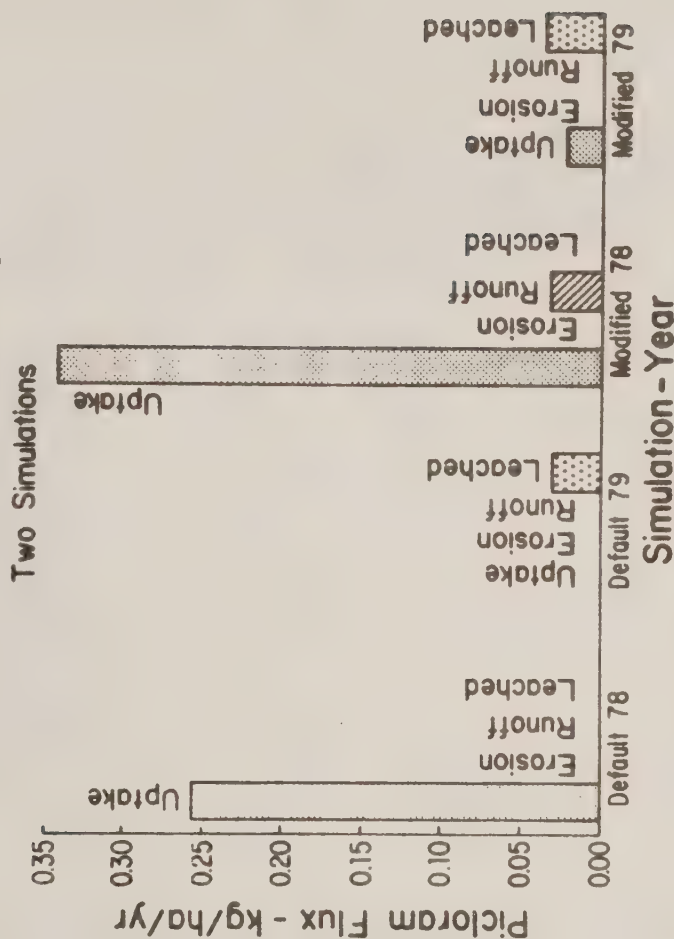
Figure 4. Pesticide flux summary for default and modified PRZM simulated picloram movement, Watershed 19, Coweeta Hydrologic Laboratory.

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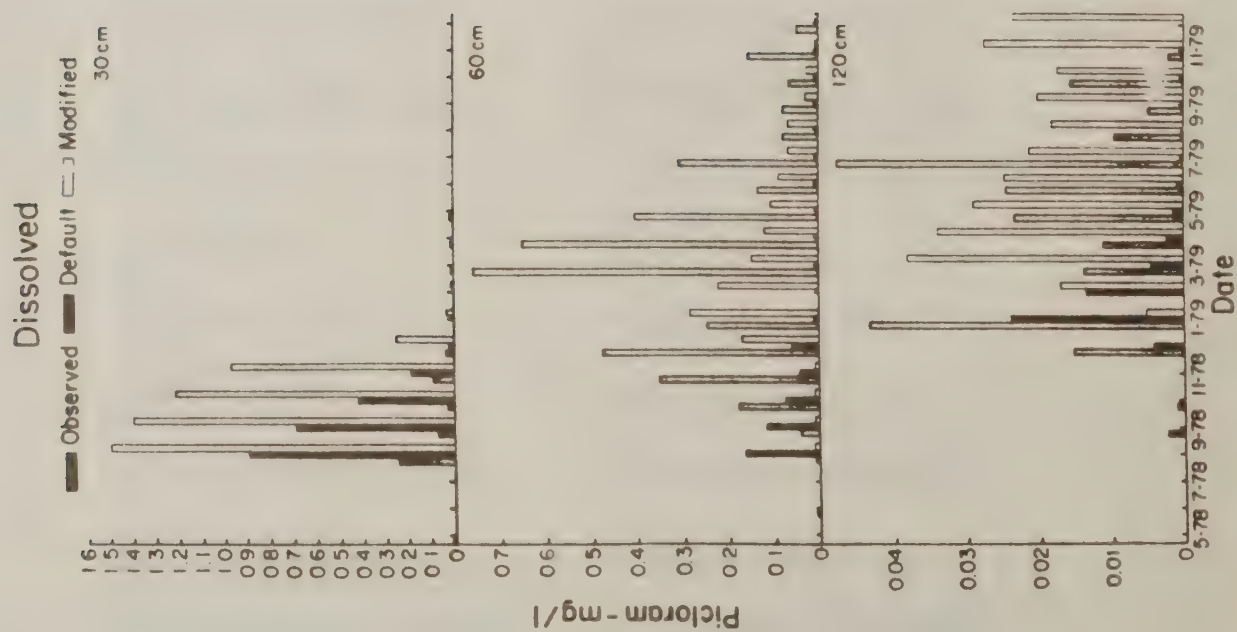
Figure 5. Comparison of default and modified
PRZM simulated picloram movement
with observed levels.
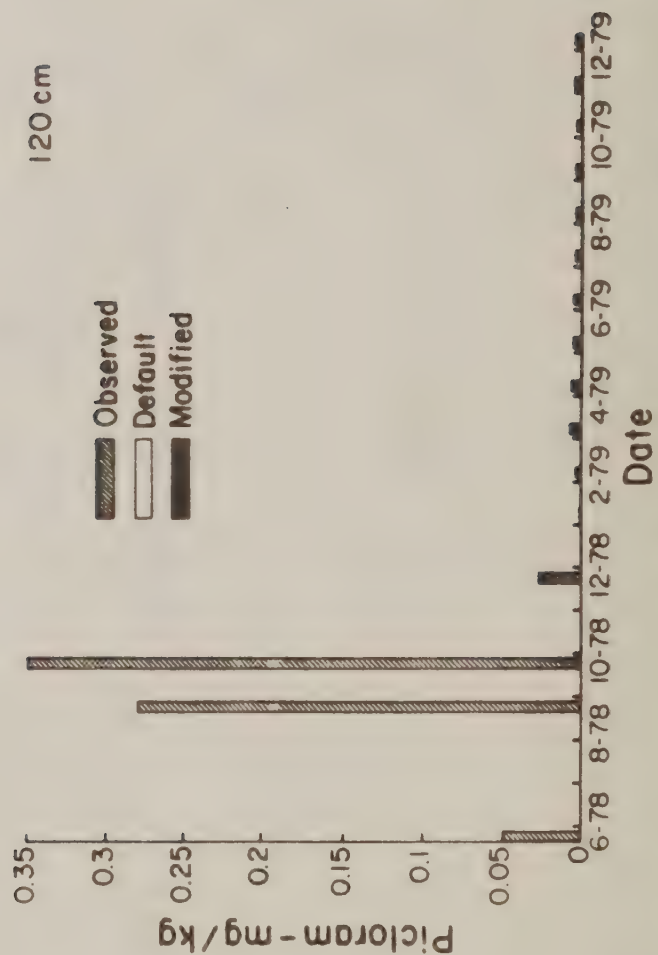
Figure 6. Comparison of default and modified PRZM
simulated picloram soil level in field data.
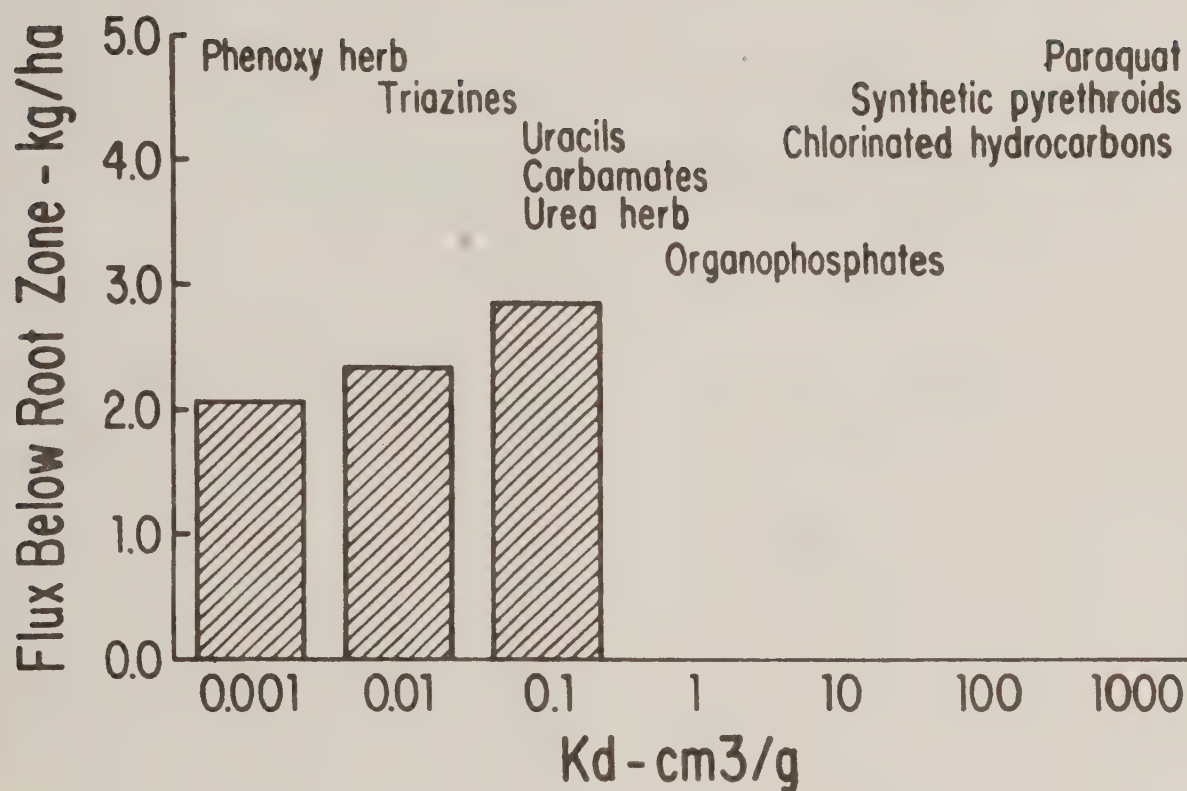
Figure 7. Changes in PRZM predictions of total leached pesticide as a function of Kd. A soil organic carbon value of 1.0 was used in calculating relative pesticide Kd values.
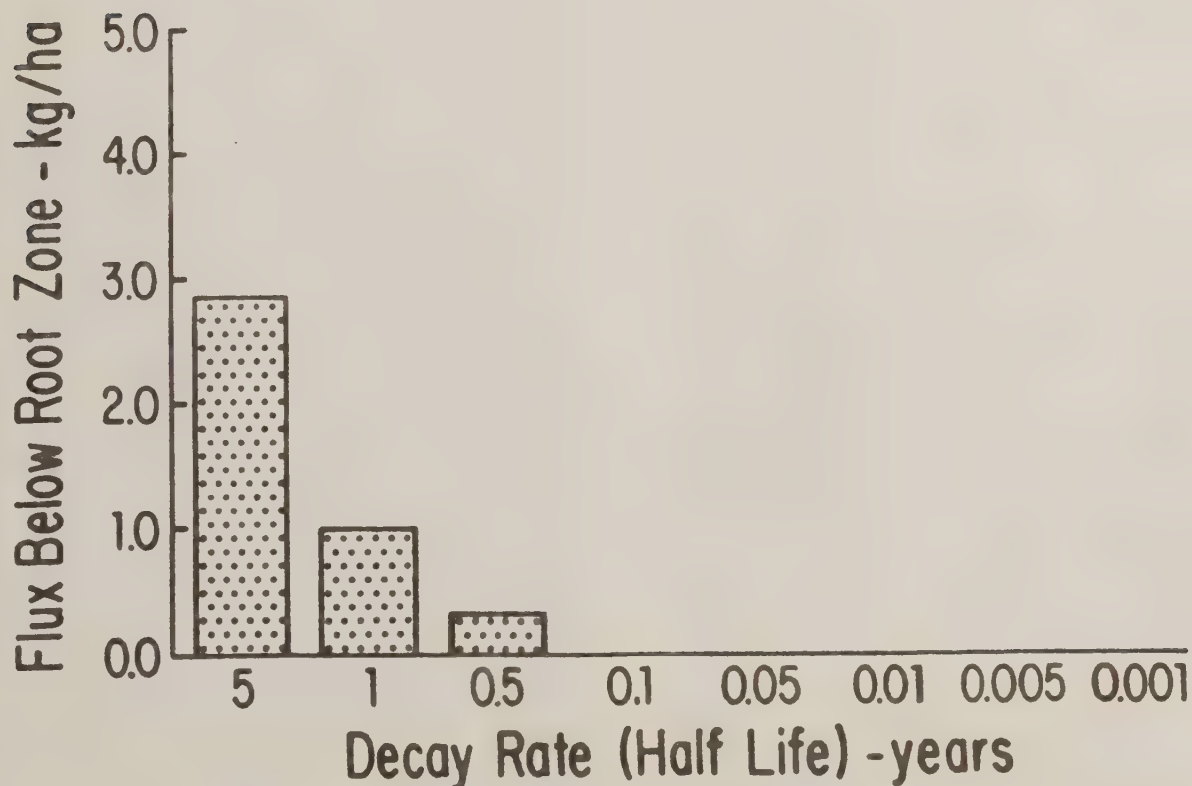
Figure 8. Changes in PRZM predictions of total leached pesticide as a function of Ks.

SIMULATION OF HERBICIDE CONCENTRATIONS IN STORMFLOW FROM FORESTED WATERSHEDS[1]

W. L. Nutter, T. Tkacs, P. B. Bush, and D. G. Neary[2]

ABSTRACT: The breakpoint rainfall hydrology and pesticide options of the field scale model CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems) were used to predict average concentrations of hexazinone [3 cyclohexyl-6-(dimethyl-amino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione] in stormflow from four forested watersheds in the upper Piedmont region of Georgia. Predicted concentrations were compared with measured concentrations recorded over a 13-month period. CREAMS accurately predicted hexazinone concentrations in the initial stormflow events which also contained the highest concentrations. The model underestimated the hexazinone concentrations in stormflow two months and greater following pesticide application. In a companion study, the daily rainfall option of the CREAMS model was used to evaluate the relative risk associated with the maximum expected concentration of hexazinone, bromacil (5-bromo-3 sec-butyl-6 methyuracil), picloram (4-amino-3,5,6 trichloropicolinic acid), dicamba (3,6-dichloro-0-anisic acid), and triclopyr $\{|(3,5,6$-trichloro-2-pyridinyl)oxy$|$acetic acid$\}$ in stormflow from small forested watersheds. The model predicted the following order of potential residue appearance in stormflow: bromacil $>$ triclopyr $>$ hexazinone $>$ picloram $>$ dicamba. Subsurface movement of residues via interflow and deep leaching losses are not simulated by the version of CREAMS used in these studies.
(KEY TERMS: CREAMS; field scale model; herbicide residue; stormflow; forests.)

INTRODUCTION

Development of new herbicides for agriculture and forestry uses has focused on producing compounds which are not only effective herbicides but also environmentally safe. Safety concerns not only human exposure hazards, but also the interactions between biodegradability, movement in the environment, and nontarget impacts as they affect productivity of local and distant ecosystems. Because of the wide range of new herbicides being developed and marketed, land managers have a need to evaluate the off-site movement potential of alternative herbicides. The availability of a usable model for evaluating pesticide movement in agricultural and forest ecosystems has been the key to developing and implementing best management practices to limit nonpoint source pollution from organic chemicals to acceptable levels.

Over the past 15 years there has been a fairly intense effort to model pesticide loss from agricultural areas (Bailey, et al., 1974; Bruce, et al., 1975; Crawford and Donigan, 1973; Haith, 1980; Knisel, 1980; Wauchope and Leonard, 1980). All of the models function on an edge-of-field basis, and most deal only with surface movement of pesticides. Most models have applications to herbicides used in forests, but none have been specifically developed for the edaphic and hydrologic conditions of forest ecosystems. In most reported field studies, maximum herbicide concentration and total amounts lost in runoff under forested conditions were less than those reported for agricultural land (Newton and Norgren. 1977; Norris, 1981; Wauchope, 1978).

A pesticide simulation model developed recently for agricultural use is CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems) (Knisel, 1980). The model is a physically based, daily simulation model that estimates stormflow, sediment transport, nutrient, and pesticide movement from field-sized areas. The pesticide submodel provides procedures to evaluate the effects of alternative chemical selection on potential pesticide residue losses in stormflow. The model's benefit to land management decision-making processes lies in its ability to provide relative comparisons among alternatives rather than to provide absolute pesticide concentration predictions. Simulation of pesticide movement by CREAMS provides total mass and storm-mean concentrations on a field-edge basis and does not provide information on downstream routing or subsurface fate (Leonard and Nowlin, 1980).

Hexazinone, symmetrical triazine herbicide, has become widely used in southern forests because it is effective in controlling a broad spectrum of annual and perennial weeds at herbicide rates tolerated by many conifers (Gonzalez, 1980; Hamilton, 1979; Michael, 1980; Neary, et al., 1981). It is manufactured under the trade name "Velpar® Gridball® Brushkiller" by E. I. DuPont de Nemours & Company. Inc., as 10 percent active ingredient (a.i.) granular and pellet formulations. (Use of trade and corporation names does not constitute

endorsement by USDA but is provided as a reference.) The selective action, ease of application, and low toxicity of the compound indicate its considerable potential as a cost-effective silvicultural tool. Off-site movement of hexazinone in storm-flow from small forested watersheds (<1 ha in size) was evaluated by field studies and reported in considerable detail by Neary, *et al.* (1983). Loss of hexazinone in stormflow over a 13-month period from four treated watersheds averaged 0.53 percent of that applied. Site-specific models of hexazinone residue behavior have been produced by Wauchope and Leonard (1980) using a power-curve function and a general concentration estimation equation.

Several interesting questions regarding simulation potential arose during the course of the hexazinone study reported by Neary, *et al.* (1983). The first had to do with how accurate a nonsite specific model like CREAMS could be. Field testing of CREAMS with atrazine and toxaphene under agricultural use showed that the model accurately reproduced field runoff data and estimated chemical residue losses within reasonable limits (15-30 percent) (Lorber and Mulkey, 1982; Steenhuis, 1979). Given that CREAMS is not designed to make absolute predictions and was designed for agricultural situations, how accurate could it predict hexazinone concentrations in storm-flow from small forested watersheds? Secondly, if the CREAMS predictions of hexazinone concentrations were adequate, how would alternative herbicides rate in terms of runoff potential on the hexazinone study site? This paper addresses both these questions and draws conclusions regarding the use of CREAMS as a management tool for assessing the impact of forest vegetation control decisions on water quality.

METHODS

The Hexazinone Field Study

The hexazinone study site is located in the upper Piedmont of the southeastern United States on the Chattahoochee National Forest of north Georgia within the drainage of Moonshine Creek, a tributary of the Broad River. A complete description of the study site is given by Neary, *et al.* (1983). Briefly, the site consists of five sub-watersheds with well-defined ephemeral channels (Figure 1). The channels are indicative of erosion induced by past agricultural practices. The watersheds are wide and bowl-shaped in their upper reaches, incised at their midpoints, and broad-bottomed in their lower reaches. The channel area in the lower reaches contain fine-textured, alluvial deposits which occasionally reach 2 m in depth. Soils on the ridges and slopes are sandy loam typic Hapludults of the Cecil series with an A horizon 0 to 10 cm thick overlying a massive B2t horizon. The A horizon increases in thickness on the slope toe.

The 60- to 80-year-old mixed pine-hardwood overstory contained scattered shortleaf pine (*Pinus echinata* Mill.), chestnut oak (*Quercus prinus* L.), white oak (*Q. alba* L.), black oak (*Q. velutina* Lam.), dogwood (*Cornus florida* L.), sourwood (*Oxydendrum arboreum* (L.) DC.), hickory (*Carya glabra*

(Mill.) Sweet), and various other species (Neary, *et al.*, 1981). The sparse understory consisted mainly of the same overstory hardwood species and various herbaceous plants.
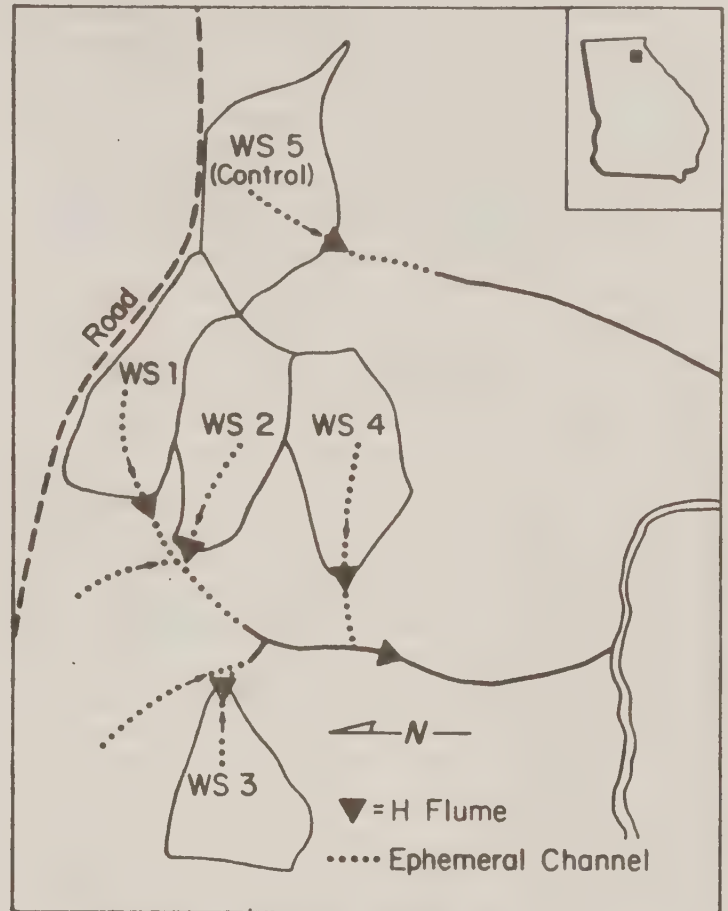

Figure 1. Watershed Locations and Stream Gauging Stations for the Hexazinone Study Area (WS 1 through WS 4 received 1.68 kg/ha a.i. hexazinone; WS 5 served as the control).

Five watersheds (WS 1 through WS 5), 0.85 to 1.09 ha in size (Figure 1), were instrumented with 30-cm H-flumes, Coshocton wheel flow-proportional samplers, analog water level recorders, and sample collection systems. All flow occurred as stormflow; i.e., at no time during the study period did baseflow occur. Standard storage and recording weighing-bucket rain gauges were installed in a clearing on a ridge to the north of WS 5.

Watersheds WS 1 through WS 4 plus some surrounding areas were treated with 1.68 kg a.i./ha of hexazinone (10 percent a.i. pellets) on April 23, 1979. Pellets containing herbicide were placed, by hand, at a spacing of 1.8 x 1.2 m to achieve the desired application rate. Because an aerial application was to be simulated, pellets were placed at the grid spacing regardless of channel location.

Water samples were collected from 26 stormflow events from April 26, 1979, to May 27, 1980, and the hexazinone

residue levels were determined as the trifluoroacetate derivative using nitrogen-selective gas chromatography (Holt, 1981).

CREAMS Computer Simulation

The CREAMS model is composed of a series of submodels linked together to yield an integrated estimate of stormflow, percolation, erosion, and dissolved and absorbed plant nutrients and pesticides. The model is physically based, does not require calibration for use, is somewhat easily understood, requires few and readily available input parameters, and represents the physical system relatively accurately (Knisel, 1980). As a field scale model, CREAMS defines a field unit as a management unit with a single land use, relatively homogeneous soils, and spatially uniform rainfall. The hydrology submodel drives the remaining submodels; i.e., the hydrologic processes provide the transport medium for sediment and chemicals.

The hydrologic section processes precipitation inputs in one of two ways to generate predicted stormflows. If daily precipitation totals are input, stormflow is predicted using the SCS runoff curve number method. If time-depth precipitation data (termed breakpoint data by CREAMS) are used, an infiltration curve based on the Green-Ampt infiltration equation is generated. Each stormflow generation procedure is discussed in detail by Knisel (1980).

Both the precipitation input options were used in this study. Breakpoint type rainfall data, i.e., hourly rainfall, measured during the course of the hexazinone application study were used to generate predicted stormflows. The simulated stormflow data were then used to drive the pesticide model to simulate hexazinone concentrations in stormflow for comparison with the field measured values. Since there was a negligible average of 400 g of sediment loss per watershed over the 13-month sampling period (Neary, et al., 1983), the erosion portion of the CREAMS model was by-passed and the stormflow results of the hydrologic model segment were passed directly to the chemical segment of the model. The model algorithms are described in detail in Knisel (1980).

In a companion study, the daily rainfall submodel was utilized to evaluate the risk to water quality by the application of five different herbicides to the forested watersheds used in the hexazinone study. For this portion of the study, 50 years of daily rainfall data were used.

The average physical parameters for the site required by both the breakpoint and daily rainfall hydrology submodels are presented in Table 1. Values were taken from published sources (Holtan, et al., 1968; Neary, et al., 1983) or calculated according to instructions in the CREAMS manual (Knisel, 1980). Required input data to the hydrology submodel other than rainfall are mean monthly temperature and radiation, watershed physical parameters, and soil hydraulic properties.

The pesticide submodel of CREAMS can account for multiple applications of the same herbicide applied to soil or foliage. The submodel allows specification of different decay rates for chemical residues placed on foliage or in the soil. Movement of pesticide below the surface one cm of soil is estimated for highly soluble compounds, but vertical and horizontal movement at greater depths over time are not simulated by the submodel. Concentrations of herbicide in solution and adsorbed onto sediments, as well as the mass transported by each process, are calculated. Pesticide residues remaining in the surface one cm of the soil residue and total pesticide loss are totaled after each storm (Leonard and Nowlin, 1980).

TABLE 1. Mean Hydrologic and Soil Physical Characteristics for the CREAMS Hydrology Submodel.

Parameter	Value	Units
Rooting depth	91	cm
Saturated conductivity	1.27	cm/hr
Field capacity (as fraction of saturation)	0.70	*
Initial soil-water storage fraction	0.75	*
Soil porosity	0.41	cm^3/cm^3
Immobile soil water content	0.17	cm/cm
Upper limit of plant available soil water storage	0.24	cm/cm
Runoff curve number	55	*
Channel slope	0.20	ft/ft
Watershed length-width ratio	0.056	*

*Non-dimensional.

The most significant input parameters into the CREAMS pesticide submodel are listed for each of the five herbicides evaluated (Table 2). Application rate and date determine the amount of herbicide exposed to storm runoff events, as this is a function of loading and rainfall frequency patterns. Solubility is an indication of a herbicide's tendency to be leached from the soil surface by infiltrating rainfall. For pesticides with a water solubility greater than one ppm, CREAMS assumes that the availability of the chemical for vertical transport with infiltrating water is described by a pesticide distribution coefficient, K_d. This coefficient is defined as the ratio of pesticide concentration in the soil to the concentration in solution at equilibrium. The main assumptions regarding K_d are that it is independent of pesticide concentration and that adsorption/desorption processes in the soil are rapid, reversible processes. Values for K_d vary with soil type, being primarily related to percent organic content or calculated specific surface of the soil (Pionke and DeAngelis, 1980). Another important pesticide parameter used in CREAMS is the decay constant, K_s. Pesticide dissipation from the surface one cm of soil is described by a simple exponential function which combines photodegradation, volatilization, microbial breakdown, and other processes. The decay constant is then used in a first-order rate expression to compute surface concentrations over time.

To evaluate runoff potential and to assess the potential risk of maximum concentrations appearing in stormflow for five different herbicides (hexazinone, bromacil, triclopyr, picloram, and dicamba), CREAMS simulations were run for each herbicide using daily rainfall records for Cornelia, Georgia (Climatological Data, National Oceanographic and Atmospheric Administration, U.S. Department of Commerce)

and the mean watershed characteristics. To generate sufficient frequency of stormflow events the hydrology and pesticide submodels were run for 50 years (1931-1980) with the specified herbicide applications repeated on the same date (May 1) each year. In this way a probability of occurrence can be associated with the concentration of herbicide in stormflow following application.

The simulation results were tabulated and the probability of occurrence for various stormflow concentrations were calculated using standard hydrologic techniques. This approach was used in an earlier study (Nutter, et al., in press) and suggested by Wauchope (1978) to evaluate potential impacts of pesticide runoff to downstream aquatic systems. The maximum annual simulated concentration for each herbicide (i.e., the annual series) was selected and the probability of occurrence for each event calculated using the Weibull plotting position formula (Viessman, et al., 1977).

The herbicide rates listed in Table 2 represent assumed loadings on the forest floor irrespective of application system or formulation. Generally, herbicides applied in liquid formulations (available for all five herbicides) have lower simulated losses than solid formulations. This results from an assumption in CREAMS that 30 percent of spray application is lost due to drift and volatilization, 60 percent is deposited on foliage, and 10 percent reaches the ground. Herbicide on foliage has a shorter half-life than herbicide in the soil and may become available to stormflow by being washed from foliage by rainfall. Since data were not available to confirm the drift-foliage-ground distributions for Piedmont forests, loadings in the CREAMS simulation were assumed to be entirely to the forest floor. Use of this assumption results in prediction of the maximum possible stormflow concentrations.

RESULTS AND DISCUSSION

Hydrology Simulation

The results of the breakpoint hydrologic simulation indicate that CREAMS generally underpredicts stormflow on an event-by-event basis (Figure 2). However, total stormflow measured over the length of the 13-month simulation (10.9 cm) exceeded the predicted value (6.2 cm) by 43 percent. The total

rainfall for the period was 2740 mm. Lorber and Mulkey (1982) found that the CREAMS stormflow prediction was 85.5 percent of observed whereas in this case predicted stormflow was only 56.9 percent of observed. Greatest disparities were on March 21, 1980 (Figure 2), when 109 mm of rain generated 1.35 cm of stormflow but was predicted to generate 0.25 cm of stormflow, and on September 18, 1980 (Figure 2), when 93 mm of rain generated 0.03 cm of stormflow but was predicted as 1.24 cm of stormflow. Closest agreement was the very large storm on November 1, 1979, when 94 mm of rain generated 1.24 cm of stormflow, predicted as 1.35 cm.
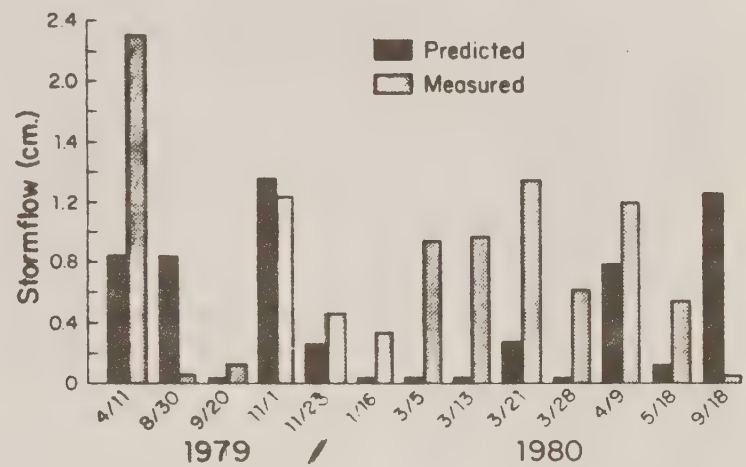

Figure 2. Mean Actual and Predicted Stormflow Volumes for Selected Stormflow Events, 1979 and 1980.

The CREAMS breakpoint hydrology model appears to be weakest in predicting stormflow from long duration, uniform intensity frontal storms. This is illustrated by a predicted cumulative stormflow of 0.03 cm for May 1980 when there was a measured cumulative stormflow of 3.81 cm from a total monthly rainfall of 432 mm. In general, predicted and actual stormflow agreed more closely for short, intense storms. The model is also insensitive to low-volume stormflow events; several (less than 0.13 cm stormflow) occurred which were not

TABLE 2. Significant Chemical and Physical Characteristics of Five Common Forest Herbicides Used as Inputs to the Pesticide Submodel of CREAMS.

Herbicide Characteristic	Unit	Picloram	Hexazinone	Dicamba	Bromacil	Triclopyr
Rate*	kg a.i./ha	0.28	1.68	0.84	6.72	1.40
Application Date	Julian	121	121	121	121	121
Water Solubility	ppm	400,000	33,000	720,000	815	410
K_d		0.7	3.0	0.077	10.0	10.0
K_s		0.0028	0.0100	0.0267	0.0046	0.0150

*Herbicide rates chosen to approximate best forest management practices for the upper Piedmont. Loadings are in kg a.i./ha reaching the forest floor irrespective of application system or formulation. Methods of estimating K_d and K_s are described in the text.

predicted by the model. CREAMS did not predict any storm-flow events until 28 days after herbicide application. The first stormflow event actually occurred three days after the application.

Percolation volume and soil water content are also predicted by CREAMS, but these values were not considered in this comparison since there is no accounting of pesticide movement in subsurface water flow except indirectly as the percolate leaves the surface layer.

Hexazinone Runoff Simulation

Outputs from the breakpoint rainfall hydrology submodel were used to drive the pesticide submodel of CREAMS. The results for the simulation of the hexazinone application and its comparison with the field measurements are shown in Figure 3. As expected, the stormflow events with the highest hexazinone concentrations were those closest to the application date. The predicted concentrations decreased over time until 150 days after application, when only small amounts of hexazinone (<0.01 ppb) were predicted to be present in stormflow. The predicted and measured concentration were similar for the first 75 days. However, between 75 and 270 days the measured herbicide concentrations remained elevated at 10 to 20 ppb. In the next stormflow event after 270 days (at 320 days), the herbicide concentration was not detectable.
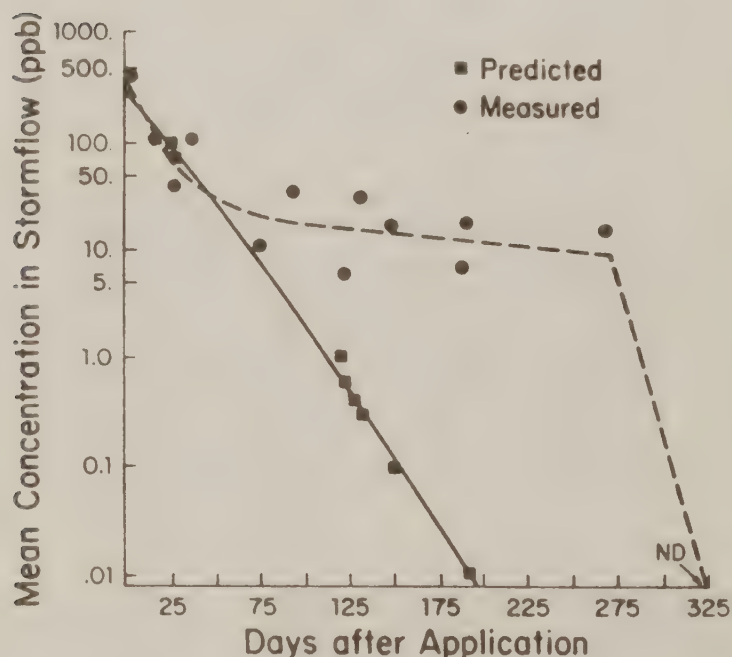
Figure 3. Mean Predicted and Actual Hexazinone Concentrations in Stormflow as a Function of Time After Application.

Predicted and actual hexazinone concentrations in the stormflow are in close agreement for events occurring less than 75 days after application. For storms occurring more than 75 days after application, the model consistently underpredicts hexazinone concentrations in stormflow. The inability to

predict hexazinone concentrations after 50 to 75 days may due to a change in the source of the hexazinone to stormflc Figure 4 shows the movement of a hexazinone pulse dov slope as measured in soil samples taken on the ridge, m slope, and base of slope. The addition of hexazinone to t ephemeral channel region from up slope could account for hexazinone concentration only slowly decreasing from day to day 275, and also account for the variability in the c centrations. Since the CREAMS model does not account movement of herbicide within the soil, it would not prec the continual supply of herbicide to the channel region.
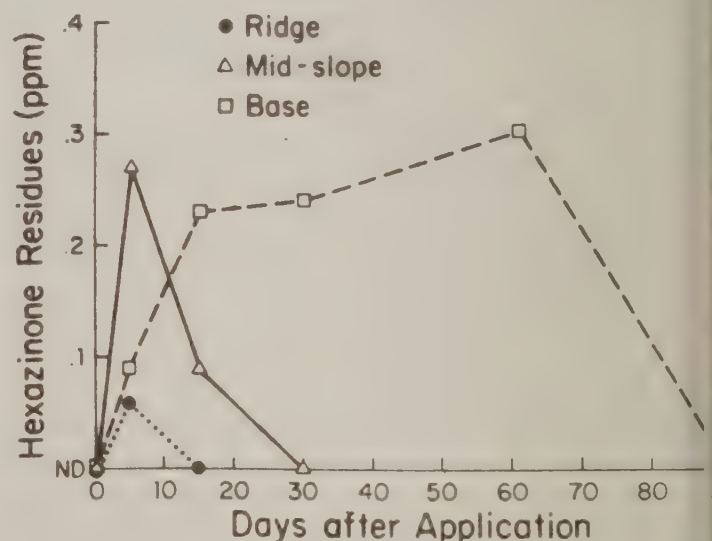

Figure 4. Hexazinone Residues (hexazinone plus metabolite A and B) in the 0-10 cm Soil Depth (after Neary, et al., 1983).

The source area for stormflow is the ephemeral stre channel and the immediate surrounding area. This is the o portion of the watershed where overland flow is likely o occur. Since CREAMS is based on the overland flow ori of stormflow, the ephemeral stream channel is most lik the source of the hexazinone residues in stormflow. Nee et al (1983), estimated that although 1.5 percent of the h zinone applied to the watersheds fell into the ephemeral str channels, 0.53 percent of the applied herbicide was tr ported off-site in the stormflow during the 397-day pe after application. The total loss predicted by CREAMS a 0.09 percent of the applied herbicide, one-fifth of that actu measured. The model apparently predicts the decline of a ability of hexazinone in the source area, but cannot inc the addition from the delayed, up-slope subsurface flow.

Another possible explanation for the higher measured centrations after 75 days shown in Figure 3 is hexazinon cycling (Neary, et al., 1983). Hexazinone is absorbed by plant roots and translocated to the site of herbicidal actic the foliage. When the leaves die they begin returning he to the forest floor via the mechanisms of throughfall and l

fall. Neary, *et al.* (1983), found the foliage in hexazinone-affected trees contained over 6 mg hexazinone/kg of leaf material. Peak leaf fall of 240 kg/ha/week produced a return of 1.4 g hexazinone/ha/week to the forest floor. Although litter fall may be a possible pathway for herbicide to become part of stormflow, it is expected that it is minor and accounts for only a small fraction.

Long-Term Herbicide Simulations

CREAMS simulations run for a 50-year period of record using the daily rainfall hydrology submodel show that bromacil, hexazinone, and triclopyr have the greatest potential of the five herbicides for movement in stormflow from the forested Piedmont watersheds (Figure 5). Bromacil concentrations declined the least as the recurrence interval decreased. This results from bromacil's tendency to bind to clay and organic matter colloids (high partitioning ratio), and hence its long residence time in the soil surface (Table 2). The concentration of bromacil simulated in stormflow can be expected to be greater than 1000 ppb at least once every 8 years (12 percent probability of occurrence). Hexazinone concentrations can be expected to exceed 100 ppb at least once every 10 years (10 percent probability of occurrence). In contrast, simulated concentrations of picloram and dicamba ($K_d < 1$) never exceeded 30 ppb (Figure 5). Thus, bromacil and triclopyr, with high K_d values and moderate-to-low solubilities, and hexazinone with a high solubility and moderate K_d value produced greatest concentrations in runoff.
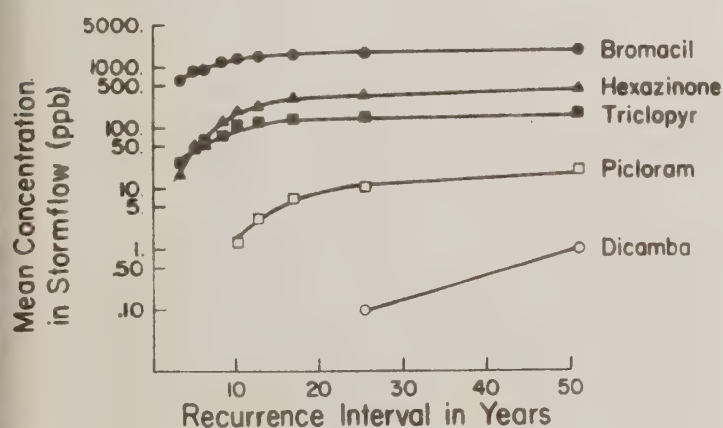

Figure 5. Reoccurrence Intervals of Maximum Annual Concentration for Various Pelleted Herbicide Applications on May 1 Each Year as Predicted From 50 Years of Stormflow and Herbicide Concentration Simulations by CREAMS.

The drop in predicted losses at $K_d < 1$ (picloram and dicamba) can be attributed to reduction in surface concentrations of pesticide due to leaching prior to stormflow. Since the partitioning ratio reflects the tendency to absorb to clay and organic matter colloids, a low K_d means a pesticide has only a weak tendency to bind to colloids. Both herbicides have negative charges and they have only a weak tendency to

bind to colloids in the acid soil and are readily leached out of the surface soil horizon. Before CREAMS calculates the pesticide available for extraction to stormflow, the amount of pesticide available is reduced by the vertical movement of pesticide out of the surface zone in the percolate. The amount removed in this way is mainly a function of K_d. Thus, herbicides with low partitioning ratios, such as picloram ($K_d = 0.7$) and dicamba ($K_d = 0.077$), will not be available in the surface zone for extraction to stormflow.

One of the limitations of CREAMS simulation of herbicide movement is that it assumes that water which infiltrates is immediately unavailable for stormflow. Dicamba and picloram are readily leached out of the surface zone and may be immediately unavailable, but it is likely that they will be picked up by interflow and return to the soil surface lower in the watershed. This subsurface movement of picloram was observed by Neary, *et al.* (1979), when picloram was applied to deep-soil, ridge-top areas of mountain watersheds in western North Carolina. At no time during the sampling was there overland flow to ephemeral stream channels. Yet water samples taken from the perennial stream below the application site showed picloram at very low levels for a short duration. Models which simulate subsurface movement of pesticides are needed to predict the impact of highly soluble chemicals such as picloram and dicamba.

All of the herbicides tested are of low toxicity to fish and wildlife. There were no simulated stormflow events which had a mean herbicide concentration close to levels that would be lethal to fish or wildlife. The closest was bromacil with a predicted high concentration of 1.8 ppm (Figure 5). Since bromacil has a 48-hour LC_{50} of 71 ppm for bluegill sunfish [(*Lepomis macrochirus* (Rafinesque)] (Mullison, *et al.*, 1979), the concentration must be increased by more than 35 times over that predicted before the LC_{50} is reached.

In conclusion, comparisons of predicted hexazinone concentrations in stormflow from forested watersheds with field data show that CREAMS, an agricultural runoff model, can be used to predict with reasonable success the herbicide concentrations in stormflow occurring shortly after application. From the standpoint of environmental impact, maximum stormflow residue concentrations occur shortly after application and CREAMS estimated those concentrations within ± 15 percent. This study confirms the conclusions of Lorber and Mulkey (1982) that the current version of CREAMS does not account for subsurface movement and thus tends to underpredict concentrations which may be influenced by subsurface interflow.

CREAMS is useful in evaluating alternative forest herbicides for their potential to appear in stormflow. The model predicts the following order of potential for appearance in stormflow: bromacil > triclopyr > hexazinone > picloram > dicamba. Highly soluble herbicides (picloram and dicamba) with low partitioning ratios (K_d) were not readily lost to stormflow. These compounds move down through the soil profile with infiltrating rainfall and are not available at the soil surface. Subsurface flow models and/or later versions of CREAMS currently under development will likely be more reliable in predicting the movement of picloram and dicamba.

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Picloram Movement in an Appalachian Hardwood Forest Watershed[1]

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ABSTRACT

Picloram (4-amino-3,5,6-trichloropicolinic acid) was applied at a rate of 5.0 kg ha^{-1} acid equivalent to 4 ha of the 28-ha Watershed 19, Coweeta Hydrologic Laboratory in western North Carolina. The herbicide was broadcast manually as a pellet formulation (10% acid equivalent) in May 1978. The objective was to eliminate a poor-quality mixed oak overstory and rhododendron (*Rhododendron maximum* L.)-laurel (*Kalmia latifolia* L.) understory prior to planting white pine (*Pinus strobus* L.). Picloram residues in samples from an Umbric Dystrochrept soil peaked in concentration in the upper 0.07 m at 11.58 mg kg^{-1}, had a half-life of about 4 weeks, and declined to near detection limits 28 weeks after application. Soil solution contained the highest picloram levels at 0.6 m (peak of 350 mg m^{-3}). Picloram residues were detected in soil solution 1.2 m into the soil, but concentrations were < 25 mg m^{-3}, and persisted for only 60 weeks. Intensive sampling of two springs detected trace levels for a period of 18 d. Only sporadic, low-level picloram residues were detected in streamflow from nested 10-ha and 28-ha watersheds during a 70-week period. Use of the herbicide picloram did not affect the quality of streamflow from Watershed 19 for domestic or agricultural purposes.

Additional Index Words: water quality, herbicide, groundwater, streamflow.

Many ridge sites in the southern Appalachian Mountains currently contain low-quality mixed hardwoods, rhododendron (*Rhododenron maximum* L.) and mountain laurel (*Kalmia latifolia* L.) in thickets of up to 18 000 stems ha^{-1}. These sites could support more productive stands of fast-growing eastern white pine (*Pinus strobus* L.) (Swank and Schreuder, 1973; Neary et al., 1984). Conversion with mechanical or manual methods is difficult and costly on these sites. Furthermore, prolific hardwood sprouting creates severe competition for newly planted pine seedlings. Prior research in the Appalachians has shown that effective competition control is necessary for successful conversion from scrub hardwoods to white pine (Swank and Miner, 1968). A promising alternative conversion technique is the use of herbicides such as picloram (4-amino-3,5,6-trichloropicolinic acid). This herbicide is manufactured by Dow

Chemical Company, Midland, MI, as the potassium salt in a 10% acid equivalent granule formulation. (Use of trade and corporation names does not constitute endorsement by USDA but is provided as a reference.) However, the water quality impacts of using picloram to convert low-quality hardwood stands to white pine are not fully understood.

Picloram has proven to be an effective herbicide for many herbicide-resistant woody plant species at rates less than the maximum-labeled rate of 9.5 kg ha^{-1} (Foy, 1975; NRCC, 1974; Peevey, 1970; Neary et al., 1979). In addition, the granular formulation is easy to apply and control. Its low toxicity to a wide range of animal species reduces the potential impacts of picloram on nontarget organisms (NRCC, 1974; Sergeant et al., 1971; Somers et al., 1974; Woodward, 1976).

Picloram losses by volatilization are negligible because of its low vapor pressure (Foy, 1975). Photodegradation occurs only when picloram is exposed directly to sunlight in aqueous solutions or on soil surfaces (Merkle et al., 1967). Leaching of picloram through the soil resembles a spreading and subsiding wave similar to nitrate and chloride. In most soils, the herbicide stays within the upper 1.2 m, but leaching can occur to greater depths in sandy soils, in soils prone to extensive cracking, or where large macropores and root channels exist (Phillips and Feltner, 1972; Rao et al., 1974).

Picloram's leaching through soil is a function of its high solubility and low reversible adsorption potential (Farmer and Aochi, 1974). Sorption is controlled primarily by soil organic carbon content, but also increases with decreasing pH and increased hydrated iron and aluminum oxide contents (Grover, 1968; Rao and Davidson, 1980; Karickhoff, 1981). Sorption of picloram can be described by the Freundlich isotherm. Several mechanisms controlling partitioning of picloram molecules between sorbed and solution phases have been proposed, but are not fully understood (Biggar and Cheung, 1973; NRCC, 1974). A more complete discussion of absorption-desorption phenomena is provided by Rao and Davidson (1980).

Since picloram formulated as both the potassium and amine salts has a high water solubility (> 400 000 g m^{-3} at 25°C), a major environmental concern with the use of picloram is possible contamination of surface water or groundwater used for irrigation. Crops such as alfalfa (*Medicago falcata* L.), sugar beet (*Beta vulgaris* L.), soybean [*Glycine max* (L.) Merr.], tomato (*Lycopersicon esculentum* Mill), and cotton (*Gossypium* spp.) are very sensitive to picloram in the range of 1 to 160 mg m^{-3} (Baur et al., 1972; Davis et al., 1968). Misapplication of picloram herbicides to surface waters or overuse in humid regions where leaching is a potential problem could lead to significant adverse nontarget impacts.
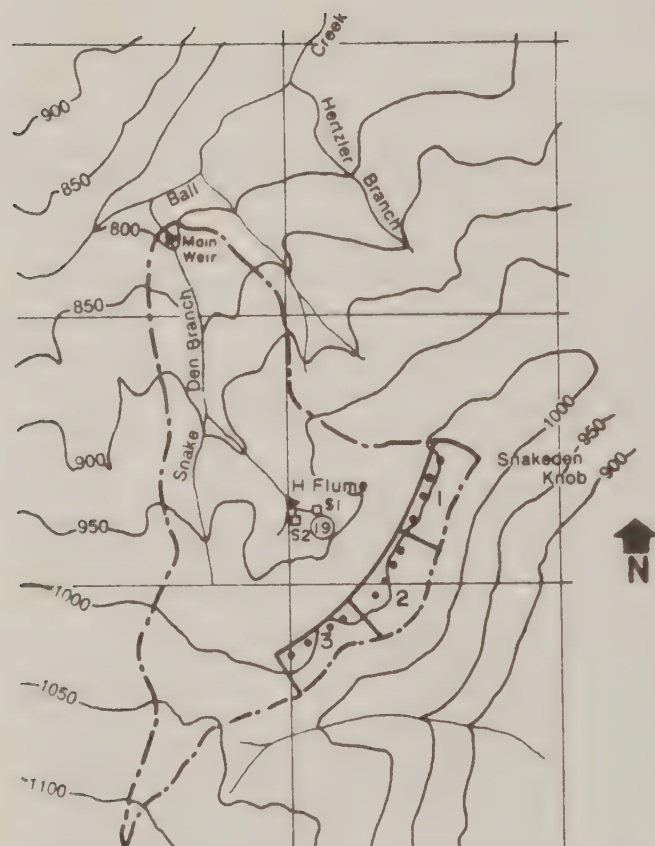
Concentrations of picloram detected in surface runoff or streamflow have varied widely in different studies. Applications of sprays at 1.1 kg ha^{-1} acid equivalent (ae) to cropland and rangeland in the South

Plot Treatment

1	5.0 kg ha⁻¹ picloram	• Lysimeter cluster
2	5.0 kg ha⁻¹ picloram	
3	Control	Scale: 1cm = 72m

Fig. 1. Picloram application area, Watershed 19, Coweeta Hydrologic Laboratory, Nantahala National Forest, NC.

Table 1. General profile description of Porters stony loam, Umbric Dystrochrepts, Watershed 19, Coweeta Hydrologic Laboratory.

Horizon	Depth	Description	pH	Permeability	Organic matter
	cm			mm h⁻¹	g kg⁻¹
O	5–0	Decomposed organic matter and leaves	4.5–5.5	50–150	
A	0–25	Very dark grayish-brown stony loam	4.5–5.5	50–150	142
Bw1	25–30	Brown stony loam	4.5–5.5	15–50	17
Bw2	30–70	Brown stony loam	4.5–5.0	15–50	13
BC	70–80	Brown loam	4.5–5.0	50–150	†
C	80 +	Saprolite, crushes to sandy loam	4.5–5.0	50–150	†

† No data.

have produced peak picloram concentrations in surface water of 90 to 2170 mg m⁻³ (Scifres et al., 1971; Trichell et al., 1968; Baur et al., 1972). In the Pacific Northwest, aerial applications of 2.2 kg ha⁻¹ ae picloram to a mixture of forests, pastures, and powerline right-of-ways resulted in short-term maximum streamflow concentrations of 20 to 78 mg m⁻³ picloram (Norris, 1969). Similar results were measured with an aerial application of picloram (1.6 to 2.3 kg ha⁻¹ ae) and 2,4-D to six brush-covered watersheds in Oregon (Norris et al., 1982). Hand applications of picloram pellets to riparian vegetation in Arizona (9.0 kg ha⁻¹ ae) on 4.5% of a forest watershed produced stormflow picloram concentrations of 52 to 370 mg m⁻³ for a period of 8 weeks (Davis et al., 1968). Considerably higher concentrations were produced by direct application of liquid picloram to Arizona and Texas streams to study dissipation downstream (Johnsen and Warskow, 1980; Mayeux et al., 1984). Initial concentrations as high as 13 720 mg m⁻³ were diluted to less than 5 mg m⁻³ over 6 km of stream distance. Drainage from a forest plot in Ontario sprayed with 0.9 kg ha⁻¹ ae picloram contained picloram levels of 38 mg m⁻³ one day after application, but still carried small but detectable (< 1 mg m⁻³) amounts 1 yr later (Suffling et al., 1974).

The purpose of this study was to examine picloram persistence and movement in mineral soil, soil solution,

springflow, and streamflow within a forest watershed in the Southern Appalachians. The study involved relatively high herbicide rates that were applied on steep topography in a heavy rainfall region of the Southern Appalachians where maximum leaching potential might be expected.

MATERIALS AND METHODS

A portion of the upper slopes of Watershed 19 (WS 19) at the Coweeta Hydrologic Laboratory in western North Carolina was selected for the study. This 28-ha, north-facing watershed ranges in elevation from 792 to 1112 m (Fig. 1). Annual rainfall averages 2054 mm, but can range from 1200 to 2500 mm. Slope, which averages 27% from the weir to the top of WS 19, is typically 35 to 40% on most side slopes, but often exceeds 100% in the upper elevations. The soils are mainly Saluda stony loams, coarse-loamy, mixed, mesic Umbric Dystrochrepts derived from pre-Cambrian gneiss, metasandstone, schist, and quartzite (Table 1). These soils have a fairly high organic matter content in the A horizon. Permeability throughout the profile is rapid, with some reduction in the B horizon. The saprolite has weathered isovolumetrically (30% porosity) and thus does not act as a restrictive layer to drainage (Velbel, 1985). Bedrock occurs at variable depths (2–5 m).

The forest stand is a mixture of low-quality hardwoods dominated by chestnut oak (*Quercus prinus* L.), scarlet oak (*Q. coccinea* Muenchh.), black oak (*Q. velutina* Lam), and hickory (*Carya* spp.). Rhododendron and mountain laurel form an almost impenetrable understory thicket (> 18 000 stems ha⁻¹) which, in some instances, prevents direct sunlight from reaching the forest floor (Neary et al., 1979). This thick understory developed from prolific sprout regrowth after a 22% basal area cut (understory only) in 1949.

On 15 May 1978, picloram herbicide was applied at a rate of 5.0 kg ha⁻¹ ae to two plots, each 2-ha in size, at the head of WS 19 (Fig. 1). To achieve uniform application, the treated area was divided into 25-m² grids and 125 g of the herbicide pellets (10% ae) were broadcast by hand onto each grid. This application rate is about average for control of hardwoods with pelleted picloram (Hamel, 1981). In comparison to where picloram is normally used in combination with 2,4-D, 5.0 kg ha⁻¹ rate used here is nine times the amount of picloram used with 2,4-D.

Hydrologic instrumentation, including water-level recorders, consisted of a 120°, V-notch weir already in place on WS 19 and a temporary 0.3-m H-flume installed at a higher elevation (Fig. 1). The H-flume was equipped with a Coshocton wheel sampler to provide flow-proportional in addition to periodic manual samples (Brakensiek et al., 1979). Two spring heads (S1 and S2, Fig. 1) were selected and deepened to provide access for sampling. The main weir, H-flume, and springs were 760, 200, and 140 m, respectively, below the downslope edge of the picloram treated area. On each of the picloram-treated and the control plots, four sets of porous cup tension lysimeters were installed 8 weeks prior to the picloram application and 15 m uphill from the lower boundary (Fig. 1). Previous research has shown that porous ceramic cups do not adsorb appreciable amounts of picloram (Rao et al., 1974). Each set contained a 0.3-, 0.6-, and 1.2-m-

deep lysimeter sampling from the Bt1, Bt2, and C horizons, respectively. Rainfall data were obtained at the permanent climate station adjacent to WS 17, from temporary storage gages located at the H-flume, and on the watershed divide.

Streamflow sampling started in May, just prior to the picloram application. Manual samples were obtained at both the main weir and H-flume weekly during dry periods, daily during wet periods, and at 1 to 6 h intervals during selected storms producing > 50 mm of precipitation in 24 h. An additional flow-proportional sample was collected continuously from the Coshocton wheel sampling system at the H-flume. Soil solution was sampled with porous cup tension lysimeters (0.02 MPa tension) on a weekly basis (Hansen and Harris, 1975). Periods of drought and winter snowpack caused gaps in the sampling record. All water samples were collected in 1-L glass jars equipped with teflon-lined caps. The bottles were thoroughly washed and rinsed with hexane and acetone prior to use in sampling. Samples were stored at 4°C and extracted for analysis within 7 d.

Mineral soil samples were collected from the two picloram-treated plots (1 and 2 in Fig. 1) after the first rainfall following herbicide application. Sampling continued until mid-December of 1978. Push-tube soil probes were used to collect increments of mineral soil from four depths (0.07, 0.15, 0.22, and 0.30 m) in the upper 0.3 m of the profile. A bucket auger was used to collect 0.1-m increment samples from depths of 0.6 and 1.2 m. Each separately-analyzed sample consisted of ten composites. Mineral soil samples were placed in labeled polyethylene bags in the field and stored frozen prior to analysis. The auger and push-tube probe were rinsed with distilled water between each sample to reduce cross contamination. The bottom and top portions of each bucket sample were also discarded to reduce sample contamination.

Both water and soil samples were transported to the Extension Pesticide Residue Laboratory, Univ. of Georgia, Athens, in insulated and ice-packed containers. Picloram in both water and soil samples was extracted with ether and analyzed by gas-liquid chromatography as the methyl ester (Anonymous, 1968; Anonymous, 1973; Bjerke, 1973). Water samples were acidified with sulfuric acid, extracted with ether and then methylated with diazomethane. Soil was mixed, subsampled, extracted with 1 M potassium hydroxide and 10% potassium chloride solvent. Following acidification, picloram was partitioned into the diethyl ether. The ether extract containing the picloram residue was further cleaned using a basic-alumina column chromatography. The picloram residues were methylated with diazomethane and quantified on a gas chromatograph equipped with a ^{63}Ni electron-capture detector. Detection limits were 0.1 mg kg^{-1} for mineral soil and 1.0 mg m^{-3} for water. Trace levels reported in water produced peaks on the gas chromatograms, but were < 1 mg m^{-3} when quantified.

RESULTS AND DISCUSSION

Residues in Mineral Soil

Picloram in the clay pellets was released starting with rainfall 10 d after application. Residues in the upper 0.07 m of mineral soil exhibited a typical dissipation pattern over a 24-week sampling period (Table 2). The initial concentration (11.58 mg kg^{-1}) was determined after the first rainfall 15 d following application. This level was higher than expected (6.0 mg kg^{-1}) based on the theoretical application rate (5.0 kg ha^{-1}). The discrepancy reflects inherent spatial variability in soil bulk density, residue distribution during application, and in sampling mineral soil for pesticide residues. Concentrations of picloram dropped very rapidly in the first 4 weeks as residues were absorbed and translocated into woody vegetation, leached deeper into the soil profile, or degraded by microorganisms. The half-life in the upper 0.07 m, based on these data, was about 4 weeks. This short half-life for picloram is typically found in warm and humid climates. In drier or colder regions, 24-week values are commonly reported (NRCC, 1974).

Table 2. Flux and percent loss of picloram below 1.2 m in a Humic Hapludult soil, Watershed 19, Coweeta Hydrologic Laboratory, May 1978 through December 1979.

	Rain		Weighted adjusted ET‡	Water available below 1.2 m†	Picloram		
Monthly	Actual	Departure from normal			Mean conc.	Flux	Loss
			mm		mg m^{-3}	mg m^{-2}	%
1978 May	39	−93	55	0	0.0	0.00	0.00
June	74	−58	117	0	0.0	0.00	0.00
July	29	−121	106	0	0.0§	0.00	0.00
Aug	313	+168	77	100	0.0	0.00	0.00
Sep	40	−82	68	0	1.6	0.00	0.00
Oct	10	−102	58	0	0.6	0.00	0.00
Nov	113	−124	34	3	0.0	0.00	0.00
Dec	185	+12	20	165	5.3	0.87	0.17
1979 Jan	319	+147	18	301	25.5	7.68	1.54
Feb	168	−15	21	147	15.4§	2.26§	0.45
Mar	101	−102	33	68	5.3	0.36	0.07
Apr	231	+84	23	208	4.1	0.85	0.17
May	169	+37	22	147	8.0	1.18	0.24
June	92	−40	88	4	8.0	0.03	0.01
July	234	+84	95	139	9.4	1.31	0.26
Aug	227	+82	90	137	2.8	0.38	0.08
Sep	197	+75	59	138	2.3	0.32	0.06
Oct	134	+22	62	72	2.8	0.20	0.04
Nov	466	+329	38	428	0.4	0.17	0.03
Dec	18	−155	9	9	0.0	0.00	0.00
Total	3159	+148	1093	2066	4.6	15.61	3.12

† Rainfall- monthly ET-accumulated ET deficit.
‡ Based on open pan evapotranspiration, solar radiation, and vegetation cover, Coweeta Hydrologic Laboratory.
§ Estimated.

The mid-June soil concentration (2.21 mg kg^{-1}) did not halve again until 12 weeks later (0.90 mg kg^{-1} in early September). Concentrations declined gradually thereafter reaching 0.06 mg kg^{-1}, close to detection limits (0.01 mg kg^{-1}), 28 to 30 weeks after application. In the upper 0.07 m of mineral soil, the concentration of picloram under these conditions decreased with time according to the site and condition specific empirical equation

$$\ln C_p = 1.6160 - 0.0626 \, T_r$$
$$+ 0.006 \, T_r^2 - 0.000002 \, T_r^3 \qquad r^2 = 0.73 \qquad [1]$$

where

T_r = days from rainfall activation of picloram pellets, and

C_p = picloram concentration in mg kg^{-1}.

Picloram concentrations deeper in the soil profile (0.15 and 0.30 m) initially followed the surface 0.07-m trend. Although initial concentrations were much lower (3.80 and 1.63 mg kg^{-1}) at both depths, concentrations also dropped by more than one-half in the first 4 weeks. Picloram levels in mineral soil at these depths continued to decline by the next sampling occurring in late June. However, by the next sampling periods in August and September, picloram concentrations actually increased by 40 to 150%. In the September sampling, concentrations at 0.15 and 0.22 m exceeded the average concentrations in the surface 0.07 m. Higher picloram concentrations deeper in the soil reflect increased leaching after particularly heavy rainfall in early August (225 mm in 4
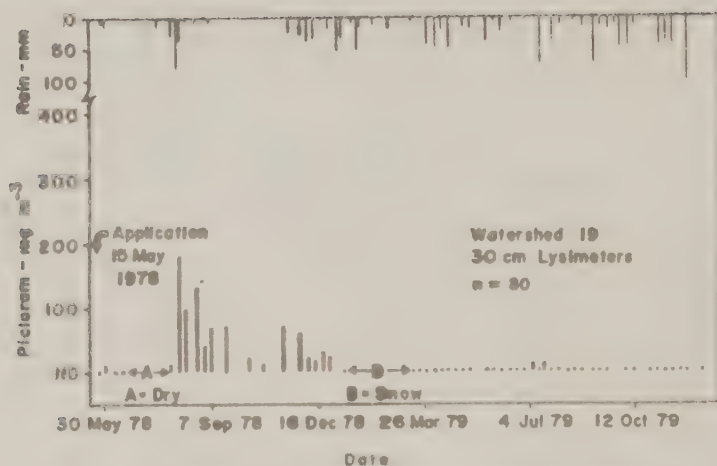
48

Fig. 2. Mean picloram concentrations in soil solution sampled at 0.3 m in a Humic Hapludult soil, Watershed 19, Coweeta Hydrologic Laboratory, 1978 and 1979.

Fig. 3. Mean picloram concentrations in soil solution at 0.6 m in a Humic Hapludult soil, Watershed 19, Coweeta Hydrologic Laboratory, 1978 to 1979.

d). Picloram residues declined thereafter reaching the 0.01 to 0.03 mg kg^{-1} range by December. At both 0.15 and 0.30 m, the measured concentration of picloram decreased according to Eq. [2] and [3]

$$0.15 \text{ m} \ln C_p = 0.5767 - 0.0436 \, T_r$$
$$+ 0.0006 \, T_r^2 - 0.000002 \, T_r^3 \qquad r^2 = 0.65 \quad [2]$$

$$0.30 \text{ m} \ln C_p = 0.4266 - 0.0400 \, T_r$$
$$+ 0.007 \, T_r^2 - 0.000003 \, T_r^3 \qquad r^2 = 0.74. \quad [3]$$

Where T_r and C_p are as defined in Eq. [1].

Mineral soil samples were not collected at the 0.60- and 1.20-m depths until late June. At that time picloram levels were 34 and 10% of the 0.07-m depth values. The same picloram wave pattern observed in the 0.15 to 0.30-m residue data showed up at 0.60 and 1.20 m. The concentration increases were larger at 0.60 m and delayed longer. The peak picloram concentration (0.86 ± 0.85 mg kg^{-1}) occurred in October and dropped to only half that level by the last sampling date. Picloram concentrations at 1.20 m remained relatively low (< 0.13 ± 0.23 mg kg^{-1}) but showed the effects of the downward leaching of the chemical.

Picloram residues measured in mineral soil samples represented the chemical adsorbed onto organic matter, mineral surfaces coated with organic matter, and clay exchange sites, plus residues in soil solution. The Humic Hapludult soils with high organic matter surface horizons (75 g kg^{-1} C) and high clay content in the subsoil were apparently effective in containing much of the picloram on the application site. On-site retention was visually evident in the treated hardwood stand by the clearly defined downslope treatment boundary.

Trees immediately downslope (60 to 100% slopes) of the picloram-treated area did not show any indication of picloram herbicidal activity. Vegetative uptake of picloram in the treated area was considerable despite dry weather conditions which limited the chemical's effectiveness (Neary et al., 1979). Picloram levels in the upper 0.3 m of mineral soil, although not determined after December 1978, were not high enough the follow-
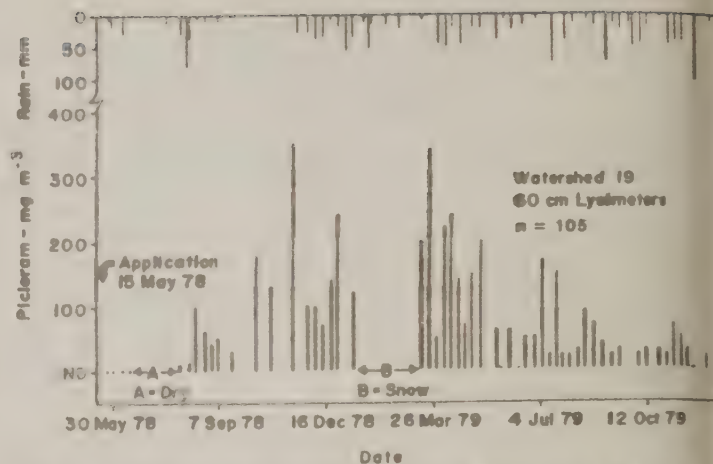
ing March to cause mortality of any planted white pine (Neary et al., 1984).

Residues in Soil Solution

Vertical movement of water due to gravity is the major mechanism for offsite movement of picloram in WS 19. Lateral flow would occur only where picloram residues reached unweathered rocks below the rhizosphere. Surface runoff is a rare phenomenon in the deep well-drained Hapludult soils of the Southern Appalachians (Hewlett and Hibbert, 1967). Also, iso-volumetric weathering of saprolite below the developed soil tends to produce deep water flow rather than shallow interflow (Velbel, 1985). Porous-cup tension lysimeters were installed to sample water just above the zone of clay (argillic) accumulation (0.3-m depth), within the argillic horizon (0.6-m depth), and in saprolite material (1.2-m depth) (Table 1).

Very small amounts of picloram were initially transported in soil solution, probably moving via unsaturated flow in the large macropores characteristic of these Umbric Dystrochrept soils at 0.3 m (Fig. 2). Droughty conditions in June and July 1978 precluded soil solution sampling ("A" in Fig. 2). Increased precipitation in August produced the highest pulse of picloram at 0.3 m (mean concentration of 174 mg m^{-3} with an individual maximum of 246 mg m^{-3}). Concentrations declined thereafter, with a smaller pulse of picloram residues in November 1978 (60–80 mg m^{-3}). During the winter months of 1979, soil solution samples were not collected because of snow conditions ("B" in Fig. 2). Sampling resumed in March 1979, but picloram residues were not detectable (detection limit 1 mg m^{-3}) until July. Then several small amounts of picloram (5–15 mg m^{-3}) were measured in soil solution at 0.3 m. Picloram residues were not detected after July 1979.

At 0.6 m, within the Bw2 horizon, picloram residues were not detected until after the summer drought ended ("A" on Fig. 3). A pulse of residues with peak concentration < 100 mg m^{-3} occurred after the early August 1978 storm. Picloram concentrations at 0.6 m declined briefly, then rose sharply in October (180 mg m^{-3}) and November (350 mg m^{-3}). An increase in rainfall
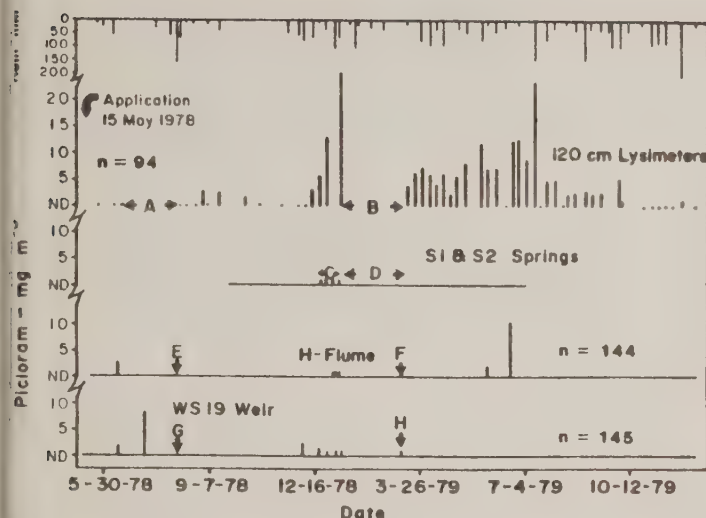
Fig. 4. Mean picloram concentrations in soil solution at 1.2 m in a Humic Hapludult soil, in springflow, and at two gaging stations, Watershed 19, Coweeta Hydrologic Laboratory, 1978 to 1979.

frequency in late November and during December kept soil solution concentrations in the 100 to 250 mg m^{-3} range until sampling stopped for the winter ("B" in Fig. 3). After sampling resumed in March 1979, picloram peaked in soil solution, with a mean concentration of 381 mg m^{-3}. Thereafter concentrations gradually declined, with frequent pulses of 100 to 200 mg m^{-3}. At the end of sampling in mid-December 1979, soil solution at the 0.6-m depth was carrying 25 mg m^{-3} picloram.

Few samples collected in the saprolite at 1.2 m contained more than 10 mg m^{-3} of the herbicide (top, Fig. 4). Picloram was first detected in early September 1978 at a concentration of 2 mg m^{-3}, but was frequently not detectable. At the end of December 1978 and during June and July 1979, mean concentrations exceeded 10 mg m^{-3}, but did not go over 25 mg m^{-3}. Picloram residues at 1.2 m were characterized by a high degree of variability, since 50% of the samples on a given date did not contain detectable levels. Also, the low picloram concentrations from 1.2 m plotted in Figure 4 at the same scale as the other two depths (Fig. 2 and 3) would appear to be mainly nondetectable and featureless. At 1.2 m, picloram residues in soil solution did show a concentration pulse pattern similar to that seen at 0.3 and 0.6 m. However, concentrations were one order of magnitude lower and delayed in time. This time lag is the same as that previously reported by Hewlett (1966) for unsaturated flow in the lower soil profile.

Picloram residues in soil solution at 0.3 m were probably affected by variability in surface application of the herbicide pellets and rapid flow in macropores. At 0.6 m, picloram concentrations in unsaturated flow were higher than at 0.3 m, since residues had more time and space to diffuse out into slower moving soil water. Evidently, the 0.6 m of soil material between the two lower lysimeter depths was sufficient to adsorb small, but significant, amounts of picloram. Concentrations at 1.2 m were at most 10% of those at 0.6 m. One hypothesis for this concentration reduction would be lateral interflow along the top of the Bt2 horizon. This process could divert soil water with higher picloram residues away from the 1.2-m-deep lysimeters and downslope into the root systems of untreated vegeta-

tion. There was no physical evidence to indicate major interflow occurred (Hewlett and Hibbert, 1967) and evergreen vegetation downslope of the herbicide treatment boundary did not show phytotoxic symptoms. Thus, the lateral movement mechanism was judged not important in reducing picloram residues in soil solution between 0.6 and 1.2 m.

Flux of picloram in unsaturated water flow in the saprolite below 1.2 m was estimated using a procedure described by Troendle and Leaf (1980). Rainfall, adjusted evapotranspiration, water available for flow below 1.2 m, and mean monthly picloram concentration were used to calculate picloram flux (Table 2). Picloram concentrations below detection limits and dry conditions precluded movement below 1.2 m until December 1978. The largest flux, according to these estimates, would have occurred in January and February 1975. Net movement of picloram was likely during all but the last month of 1979. The total estimated loss below 1.2 m, 3.12% of the applied picloram, agrees with losses of herbicides reported elsewhere (Wauchope, 1978).

Springflow Residues

A major water quality concern with picloram is its high solubility and potential to move offsite into streams or groundwater. Thus, two springs (S1 and S2) below the picloram-treated area were sampled to determine if residues were migrating downslope in saturated flow at the saprolite-bedrock interface (Fig. 1). These two springs, 140 m downslope of the picloram-treated area, mark the beginning of perennial flow for 40 to 50% of the eastern side of WS 19. Such springs are sometimes used for domestic sources of water in the Appalachian Mountains. Flow from both springs is eventually routed through the H-flume to the main gaging station (Fig. 1).

Both springs were deepened to enable sample collection and to observe flow from the saturated soil mantle. Neither spring was measured to determine flow rates. Sampling started in October 1978 on a weekly basis.

No picloram residues were measured until 20 December 1978 when traces of picloram began appearing. Trace levels were present in S1 or S2 until 8 January 1979 ("C" in Fig. 4). The sampling frequency was increased to once every 2 to 3 d, from early January to late March 1979 ("D" in Fig. 4). Twenty-eight samples were collected from both S1 and S2 during this period and no additional picloram residues were detected in springflow. Sampling resumed at a normal weekly or biweekly interval until July 1979 when springflow sampling ceased. During this period also, picloram residues were not detectable in either spring.

During the 40 weeks that springs S1 and S2 were monitored, picloram residues were present in only trace levels for a period of 18 days. In terms of water quality impacts, there was no adverse effect on the quality of the springs. The residue levels were below those needed to impact the most sensitive vegetable crops (1 to 10 mg m^{-3}) and were short in duration. No human exposure standards have been set by the Environmental Protection Agency for picloram residues in water because of the compund's low toxicity and lack of bioaccumulation (Anonymous, 1976). A chronic SNARL (Suggested No

Table 3. Mean picloram residues in a Typic Hapludult soil during 27 weeks after application, Watershed 19, Coweeta Hydrologic Laboratory.

Depth	Picloram concentrations in mineral soil						
	31 May 1978†	12 June 1978	26 June 1978	14 Aug. 1978	8 Sept. 1978	5 Oct. 1978	18 Dec. 1978
m	mg kg⁻¹						
0.07	11.58 ± 1.19‡	2.21 ± 0.77	1.31 ± 0.44	1.27 ± 0.62	0.90 ± 0.37	0.34 ± 0.05	0.06 ± 0.03
0.15	3.80 ± 3.05	1.42 ± 0.48	1.17 ± 0.43	0.83 ± 0.29	1.16 ± 0.34	0.75 ± 0.35	0.03 ± 0.01
0.22	¶	0.98 ± 0.21	0.49 ± 0.07	0.80 ± 0.45	1.23 ± 0.31	0.34 ± 0.12	0.01 ± 0.01
0.30	1.63 ± 1.33	0.45 ± 0.23	0.38 ± 0.12	0.62 ± 0.25	0.81 ± 0.28	0.53 ± 0.19	0.01 ± 0.01
0.60	¶	¶	0.45 ± 0.44	0.08 ± 0.06	0.48 ± 0.26	0.86 ± 0.43	0.40 ± 0.28
1.20	¶	¶	0.13 ± 0.12	ND ± 0.00§	0.11 ± 0.09	0.01 ± 0.01	

† Sampling date 1 d after first rain. Application date 15 May 1978.
‡ Means ± standard error.
§ Detection limit 0.01 mg kg⁻¹.
¶ Samples not taken at this depth.

Adverse Response Level) of 1050 mg m⁻³ has been recommended by the Safe Drinking Water Committee of the National Research Council (NRC, 1983). The tolerance level for milk (50 mg m⁻³) is 50 to 100 times the levels observed in springflow. By comparison, the tolerance level for 2,4-D in municipal water supplies is 100 mg m⁻³.

Residues in Streamflow-10 ha Watershed

Picloram movement in streamflow was monitored at an H-flume sampling station below the herbicide treated area and the 120° V-notch weir at the base of the watershed (Fig. 1). These two streamflow gaging stations encompass watersheds of 10 and 28 ha, respectively. Mean daily flows at the H-flume were 0.007 to 0.011 m³ s⁻¹ km⁻² in low flow periods (October-November) and 0.033 to 0.109 m³ s⁻¹ km⁻² in high flow periods (March–April). The instantaneous peakflow at the H-flume (0.296 m³ s⁻¹ km⁻²) occurred during the early August 1978 storm, which was the first major storm event after picloram application (Fig. 4).

At the H-flume, two sampling techniques were employed. A Coshocton wheel attached to the flume produced a 0.5% flow-proportional sample. In addition, grab samples were collected weekly or on a more frequent basis as conditions warranted. Of 75 samples collected on a flow-proportional basis between 22 May 1978 and 14 September 1979, only one sample had a trace of picloram. As will be shown with manually-collected samples, picloram residue pulses were so sporadic and so low in concentration that the flow-proportional bulking process diluted any picloram levels below detection limits. Data from the H-flume presented in Fig. 4 are from the manually collected discrete samples rather than the flow-proportional ones.

Of 144 discrete samples collected at the WS 19 H-flume, only a few had any positive picloram residues (Fig. 4). One, on 9 June 1978, contained 3 mg m⁻³ picloram. Except for several samples in early January 1979, picloram residues in streamflow at the flume did not show any pattern related to residue levels higher up in the watershed.

A series of frequent samples were collected at the H-flume during the rainfall in early August which constituted the first major storm event after the picloram application in May ("E" in Fig. 4). One sample was taken daily from 1 through 6 August. Then, five samples were collected on 7 August 1978 at 2- to 4-h

intervals from 0800 to 1915 hours during the peak stormflow of this entire study. Daily sampling resumed during the period of 8 August through 10 August. Throughout all this intensive sampling no picloram residues were detected in streamflow.

Samples continued to be negative for picloram until January 1979 when three consecutive samples on 2, 3, and 8 January had trace levels. During March, another set of closely-spaced samples was collected daily from 2 March through 9 March 1979. However, all samples were negative for picloram residues ("F" in Fig. 4). Only two more samples, collected on 30 May and 20 June 1979, had picloram levels of 2 and 10 mg m⁻³, respectively. The appearance of these two small pulses could be related to an additional flux of picloram out of the soil system in May (Table 3). Another flux of picloram in July 1979 did not produce detectable residues at the H-flume. Sampling through mid-December 1979 failed to turn up any additional picloram.

Residues in Streamflow- 28-ha Watershed

Streamflow samples collected further downstream at the main weir on WS 19 (Fig. 1) showed the same pattern as that observed at the H-flume (Fig. 1). A total of 145 discrete samples were collected manually between 12 May 1978 and 13 December 1979. A small amount of picloram (2 mg m⁻³) was measured in a sample collected 3 d after (12 June 1978) the one which was positive at the H-flume (3 mg m⁻³). Another sample collected in early July had 8 mg m⁻³. Both of these samples were collected after rainfall (Fig. 4) but were not associated with significant residue movement elsewhere in the watershed. The latter peak may have passed through the H-flume but was missed by the grab sampling and diluted by the continuous flow-proportional sampling. Intensive sampling ("G" in Fig. 4) during the August storms, similar to that described for the H-flume site, did not turn up any picloram residues.

A series of samples collected at the WS 19 weir in December 1978 and January 1979 contained intermittent picloram residues in the trace to 2 mg m⁻³ range. Streamflow samples thereafter were mostly free of picloram. One sample taken during intensive sampling in March 1979 ("H" in Fig. 4) contained a trace amount of picloram.

Although very low-level residues of picloram were detected at the WS 19 weir and probably continued on into Ball Creek, they were so infrequent and at such low

levels as to have no adverse effect on the quality and subsequent uses of water downstream. Mixing of flow from the WS 19 stream (Snake Den Branch) with flow from the larger Ball Creek (Fig. 1) would undoubtedly reduce the observed concentrations of picloram well below detection limits.

CONCLUSIONS

The application of a pellet formulation of picloram to 4 ha of ridge and upper slopes of a 28 ha Appalachian Mountain forest watershed did not produce any adverse affect on water quality within the 2 years of the study. Picloram in the upper 0.07 m of mineral soil exhibited a very short half-life (4 weeks) compared to other reported values. Concentrations in the upper 0.3 m of mineral soil were close to detection limits after 28 to 30 weeks. Although soil solution concentrations reached 381 mg m^{-3}, picloram was at or near detection limits some 60 weeks after application. These high concentrations did not carry on downslope in springflow or streamflow. Residues of this highly soluble, and hence mobile, herbicide were observed considerable distances (700–800 m) downstream. However, levels were low (10 mg m^{-3}) and very sporadic.

There has been considerable concern about the use of picloram for silvicultural treatments in the high rainfall zone of the Appalachians. The picloram application rate used in this study was 9 times that of the most commonly used picloram forest-use herbicide (2,4-D plus picloram). When used at rates established on the product label in accordance with special use precautions and well away from flowing streams, picloram should not pose any threat to water quality. The pelleted formulation is easy to control during application and thus less susceptible to accidental movement into streams. In addition, picloram is very low in toxicity to aquatic fauna. Use of picloram as described in this study is one alternative for site preparation and weed control in the steeplands of the Appalachian Mountains. We believe that this method is practical, does not disturb soil, and does not pose a significant adverse impact on the aquatic environment and water quality.

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Off-Site Movement of Hexazinone in Stormflow and Baseflow from Forest Watersheds[1]

DANIEL G. NEARY, PARSHALL B. BUSH, and JAMES E. DOUGLASS[2]

Abstract. Four forest watersheds (1 ha each) in the upper piedmont of Georgia were treated with hexazinone [3-cyclo-hexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione] pellets[3] at a rate of 1.68 kg ai/ha. From the end of April, 1979, until May, 1980, 26 storms were monitored to determine movement of hexazinone and two of its metabo-lites [A: 3-(4-hydroxycyclohexyl)-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione, and B: 3-cyclo-hexyl-6-(methylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-di-one] in runoff water. Residues in runoff peaked in the first storm after application (mean concentration of 442 ± 53 ppbw), and declined with subsequent storms in a power curve function: Conc. (ppbw) = 405 × rate × $(1 + 0.44 \times$ days$)^{-1.1}$. Loss of hexazinone in storm runoff averaged 0.53% of the applied herbicide, with Storms 1 and 17 ac-counting for 59.3% of the chemical exported. Storm 1 had high residue concentrations and low runoff volume, while Storm 17 contained only low residue levels but a very large stormflow. Hexazinone was the predominant compound in the runoff of all 26 storms. Metabolites A and B occurred in runoff in low-to-trace concentrations (<23 ppbw) for up to 7 months after application. Subsurface movement of hexazinone appeared in streamflow 3 to 4 months after application and produced an additional loss of 0.05%. A second-order perennial stream below the treated watersheds periodically contained hexazinone residues of <44 ppbw.

Additional index words. Residue, herbicide, ecosystem model, runoff.

INTRODUCTION

Development of new herbicides for agricultural and forestry uses has focused on two primary topics, efficacy and safety (17). Safety concerns not only applicator and other human exposure, but also biodegradability, movement in the en-vironment, impacts on wildlife, target species selectivity, and effects on the protected crop. Clearly, the ideal herbi-cide is one which is effective, is applied in an easy-to-handle formulation, is biodegradable, has a low toxicity to animals, and does not move off-site. The first four characteristics can be adequately assessed under controlled laboratory con-ditions. The fifth feature can be approximated with labora-tory microcosms and models. The validity of any model predicting herbicide movement in ecosystems however, must be verified with systematic field evaluations.

The considerable body of information on herbicide and insecticide residues leaving agricultural fields has been re-viewed by Wauchope (29). He noted several interesting gener-alizations which applied to 22 studies involving 32 chemicals. Pesticide runoff events were classified into critical (1 cm of rain within 2 weeks of application producing the bulk of runoff losses), catastrophic (a storm event removing >2% of the applied chemical), and high-low (high pesticide con-centration but low runoff volume). Most pesticides lost were in the solution phase and, excluding wettable powders and persistent compounds, total loss of pesticides from fields was generally 0.5% or less.

Over the past 10 yr there has been a fairly intense effort to model pesticide loss from agricultural areas (1, 4, 5, 7, 8, 12, 18, 30). All of the models function on an edge-of-the-field basis. Until recently, little research has been directed towards modeling the downstream fate of pesticides. Most models have application to forest pesticide use, but none have been developed specifically for the edaphic and hydrologic conditions of forest ecosystems. In addition, the literature contains few references to replicated data sets on pesticide movement in storm runoff from forest ecosystems (6, 9, 23, 24, 25, 26, 27). In most reported instances, maximum con-centrations and total amounts lost in runoff under forested conditions were less than those reported for agricultural land (29).

Hexazinone is a recently-developed, symmetrical triazine herbicide which is effective in controlling a broad spectrum of annual and perennial weeds at herbicide rates tolerated by many conifers. The 10% ai pellet formulation (2 and 0.5 cm^3 sizes) and the 20% ai formulation (1 cm^3 size) were recently registered for non-crop and reforestation areas, and have considerable potential as cost-effective tools in pine silviculture (2, 11, 13, 20, 22). In addition, the pellet formulation and low toxicity reduce potential nontarget organism impacts (10, 16).

High water solubility (33000 ppmw at 25 C) makes hexa-zinone susceptible to off-site movement in storm runoff and leaching[4]. Lateral or vertical movement in soil is slowed by high organic matter or clay cation exchange capacity. Hexazinone is subject to microbial degradation but resists photodegradation. Miller and Bace (21) reported high hexazinone concentrations (up to 2400 ppbw) from direct fall of pellets into a forest stream during an aerial application

in Alabama. Concentrations fell to 110 ppbw within 24 h and to <20 ppbw after 10 days.

This study was established to determine: a) the off-site movement of hexazinone in storm runoff from small forest watersheds; and b) the extent of dilution of the chemical downstream from the treated areas.

MATERIALS AND METHODS

Site description. The study site is located in the Chatta-hoochee National Forest, 10 km southeast of Clarksville in northeast Georgia. It lies within the drainage of Moonshine Creek, a tributary of the Broad River. The site consists of a series of well-defined, ephemeral drainages at the 400- to 450-m elevation. Ridge tops are broad and show evidence of extensive erosion induced by past agriculture. The drainages are typically broad, bowl-shaped in their upper reaches, deeply eroded at their midpoints, and broad-bottomed in their lower reaches. Maximum relief from ridgetop to peren-nial stream averages 50 m. The original stream bottoms are buried under fine-textured alluvial deposits which reach 2 m in depth. Moonshine Creek alternates from low gradient sections with sandy bottoms to steep ones with rocky riffles, pools, and waterfalls.

The soils on the ridges are sandy loams of the Cecil series (Typic Hapludults). These well-drained soils have formed from mica-rich gneiss and schist of the pre-Cambrian Tallulah Falls formation. Upper ridges contain eroded phases of the Cecil series with a remnant A horizon (0 to 10-cm thick) overlying a massive B 2t horizon. The A horizon increases in thickness on the slope toe. Bottomlands surrounding the headwater ephemeral and perennial streams are colluvial in nature.

The 60- to 80-yr-old mixed pine-hardwood overstory is characterized by scattered shortleaf pine (*Pinus echinata* Mill.), chestnut oak (*Quercus prinus* L.), white oak (*Q. alba* L.), black oak (*Q. velutina* Lam.), flowering dogwood (*Cornus florida* L.), sourwood [*Oxydendrum arboreum* (L.) DC.], pignut hickory [*Carya glabra* (Mill.) Sweet], and various other species (22). Hardwood growth is poor on the ridges and good in the stream bottoms. The sparse understory consists of overstory hardwood species and various herbaceous plants.

Instrumentation. Five watersheds (designated WS 1 to WS 5), 0.85 to 1.09 ha in area, were selected and surveyed in early March, 1979 (Figure 1). These watersheds produce flow only during storm events. They were instrumented in April, 1979, with 30-cm H-flumes, Coshocton wheel flow-proportional samplers, analog water level recorders[5], and sample collection systems (3). The flow-proportional

samplers were designed to collect approximately 0.5% of the total flow through the H-flumes. Runoff samples were routed by pipe to two 100-L polypropylene storage con-tainers. The water level recorders produced a continuous trace of water head in the H-flume which was translated into total discharge using a standard rating equation and processing program (15). Storage and recording rain gauges[6] were installed in a clearing on a ridge north of watershed WS[5].

Watersheds WS 1 through WS 4 were selected for herbi-cide treatment because storm runoff from these watersheds converges into the same drainage (Stream A, Figure 1). Over much of its length, this stream alternates from open-channel flow to subsurface flow in recent alluvium. Stream A was instrumented, below the point of convergence of drainage from watershed WS 4 and Stream A, with a cutoff wall, H-flume, and water level recorder, but no flow proportional sampler (No. 87). This monitoring station (No. 87, Figure 1) was established to determine if hexazinone or its metabolites would leach deep into the soil, bypass the H-flumes, and then move downstream. Water sample collection began in May, 1979, and flow measurements were started in June.

In April, 1979, a sampling and stream gauging station (No. 88, Figure 1) was established on Moonshine Creek about 30 m downstream of its confluence with Stream A.
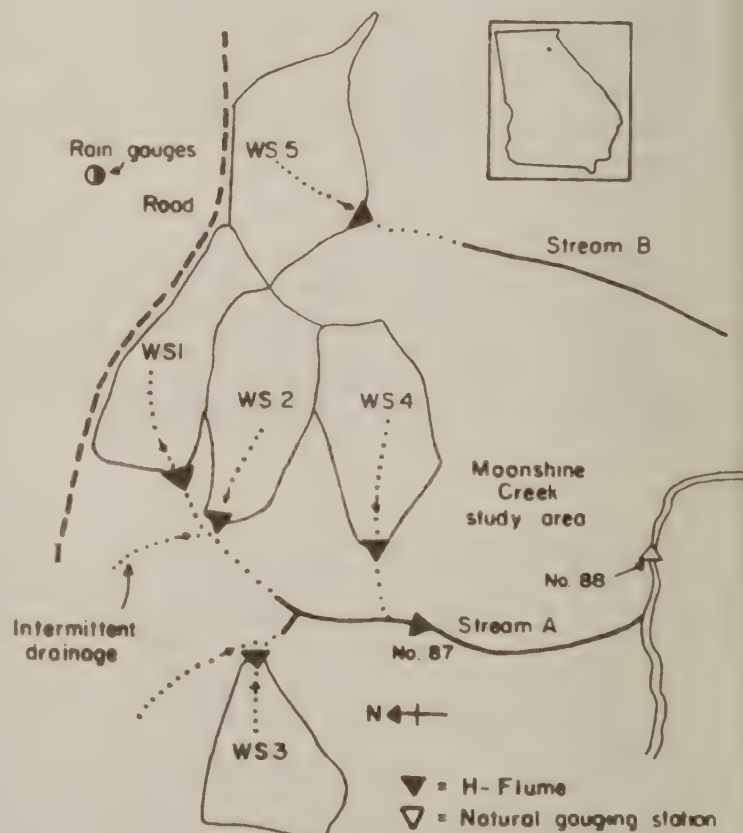

Figure 1. H-flume locations and stream gauging stations, Moon-shine Creek study area (watersheds WS 1 through WS 4 received 1.68 kg ai/ha hexazinone, WS 5 served as control).

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A solid rock-bottomed channel, suitable for rating water discharge, was instrumented with an analog water level recorder and automatic water sampler. A staff gauge was installed in the stream, and a rating developed from stream-velocity measurements taken weekly and during selected storms.

Treatment. Watersheds WS 1 through WS 4, plus some surrounding areas, were treated with 1.68 kg ai/ha of hexazinone (10% ai pellets) on April 23, 1979. Pellets were spread at a spacing of 1.8 by 1.2 m to achieve the desired application rate. Wire flags were used to mark pellets for later sampling of mineral soil, and to tally pellets which fell into the ephemeral drainage channels.

Water and sediment sampling. Runoff water samples were collected with the flow-proportional Coshocton wheels during each of 26 storms between April 26, 1979, and May 27, 1980. Several long-duration storms were repeatedly sampled and some exceeded the storage system capacity. Water samples collected at the No. 87 flume on Stream A were all discrete, manually-collected samples taken under baseflow conditions rather than during storm runoff (28). Water samples collected at No. 88, from Moonshine Creek, were either discrete or bulk samples depending on the type of sampler in operation.

Water samples were removed from the sampling systems immediately after storms and put into 1-L washed and methanol-rinsed glass jars. The samples were stored at 4 C and transported in insulated, ice-packed containers to the University of Georgia where they were stored at 4 C prior to herbicide extraction and analysis. Duplicate samples retained for residue cross-check analysis were frozen in 1-L polypropylene bottles. Bedload sediment, which accumulated during several severe storms, was collected to determine total sediment mass and herbicide-residue content.

Soil samples. Litter and mineral-soil samples were collected 3, 14, 30, 60, and 90 days after the first rain following herbicide application. During the hexazinone pellet spreading, the location of individual pellets was marked with flagging to locate future sampling points. Litter and mineral-soil samples were obtained from three positions, 60 cm in distance from pellets marked for the given sampling date, and composited. Samples were also separated by topographic position (ridge, mid-slope, and toe) on each of the four treated watersheds. Litter was collected first, and then mineral soil cores were removed in 10-cm increments to a depth of 30 cm. Soil and litter material were frozen prior to residue analyses.

Hexazinone residue analyses. Water, soil, and litter samples were extracted with chloroform and ethyl acetate, and the amounts of hexazinone and its metabolites were determined by nitrogen-selective gas chromatography after reaction

of metabolites with trifluoroacetic anhydride (16). The derivatives were analyzed on the same day as derivatization[7]. The gas chromatograph was operated under the following conditions: inlet temperature 230 C; detector temperature 280 C; helium carrier gas flow 35 cc/min. The column was temperature-programed from 230 to 280 C at a rate of 10 degrees/min, and was held at the final temperature for about 8 min. Hexazinone and metabolite levels were determined by comparison of peak heights with those of known analytical standards[8]. A reagent blank and sample of known hexazinone and metabolite content was included in each set of analyses, and results were corrected for percent recovery. The detection limit for hexazinone and both metabolites was normally 1 ppbw for water and 0.1 ppmw for soil and litter.

RESULTS AND DISCUSSION

Precipitation and storm runoff. Rainfall 3 days after the hexazinone pellet application produced the first of 26 runoff events. Mean storm discharge for watersheds WS 1 through WS 4 ranged from a low of 0.05 m^3 for Storm 11 to a high of over 172 m^3 for Storm 17 (Table 1). By contrast, flow from the untreated control watershed (WS 5) ranged from none for Storms 1 and 2, to nearly 81.5 m^3

Table 1. Rainfall and mean storm runoff for 26 storm events in four upper-piedmont watersheds, April 26, 1979, to May 21, 1980.

Date of storm	Storm no.	Amount of rain	Mean storm runoff	
			Area-depth	Volume
		——— (mm) ———		(m^3)
1979				
April 26	1	50	0.6	5.67 ± 3.43
May 10	2	47	0.2	2.24 ± 1.72
May 21	3	55	0.8	7.23 ± 2.23
May 31	4	34	0.4	3.42 ± 2.43
July 8	5	72	0.1	1.23 ± 1.83
July 12	6	13	<0.1	0.81 ± 1.17
July 23	7	38	<0.1	0.20 ± 0.20
July 26	8	55	0.3	3.20 ± 3.31
Aug. 25	9	70	0.2	1.70 ± 0.43
Sep. 3	10	70	0.6	5.47 ± 3.79
Sep. 18	11	11	<0.1	0.05 ± 0.00[a]
Sep. 21	12	55	2.0	18.87 ± 4.55
Sep. 28	13	43	0.2	1.45 ± 2.62
Oct. 4	14	25	<0.1	0.50 ± 0.88
Oct. 23	15	11	<0.1	0.10 ± 0.06
Oct. 30	16	44	0.4	4.27 ± 3.28
Nov. 2	17	94	18.2	172.38 ± 55.15
Nov. 10	18	35	0.2	1.52 ± 1.45
Nov. 25	19	93	5.1	48.79 ± 7.68
1980				
Jan. 18	20	92	5.5	52.49 ± 16.50
March 7	21	107	11.4	107.84 ± 14.63
March 17	22	128	12.0	114.13 ± 14.51
March 20	23	111	16.8	159.43 ± 30.72
March 28	24	62	6.7	63.61 ± 9.17
April 12	25	87	10.1	95.65 ± 18.90
May 21	26	82	4.4	41.48 ± 8.78

[a]Estimated storm runoff due to equipment failure.

for Storm 17. Total flow for the control watershed for the period April 26, 1979, through May 27, 1980, was 37% of the mean for the treated watersheds. Some of this difference was due to inherent variability of these small watersheds, and the remainder due to increased runoff on the treated watersheds after elimination of the hardwoods.

Storm 17 in early November produced 94 mm of rain in 13 h. A storm of this size is expected to occur once every 2 to 5 yr in north Georgia (14). This storm included a downpour of about 25 mm in 1 h and accounted for 75% of the mean discharge from the treated watersheds over the duration of the first 17 storms. The probability of this size storm occurring during the hexazinone application months of April and May is relatively high (p = 0.015 to 0.02 compared to P< 0.01 in the month it actually happened (14).

Rainfall during 1979 set new records in north Georgia, with an excess of 30% recorded at some stations. Annual rainfall in the area is usually 1300 to 1400 mm. The yr 1980 remained wet through May with precipitation 31% above average due to record rainfall in March (441 mm, 162% of average). Three storms during this unusually wet month accounted for 41.4% of the total runoff recorded during the course of the study.

Hexazinone and metabolite concentrations. The mean concentration of hexazinone in storm runoff followed a typical residue decay curve. The peak concentration for the four treated watersheds averaged 442 ± 53 ppbw and occurred with Storm 1, three days after the herbicide application (Table 2). The maximum concentration, 514 ppbw, occurred in runoff from watershed WS 3. Hexazinone concentrations declined sharply in Storm 2 runoff 2 weeks later, dropped even further in Storm 3, climbed again in runoff 40 days after application (Storm 4), and thereafter stayed below 34 ppbw. Except for Storms 1 and 4, the coefficient of variation (CV) in hexazinone concentrations between watersheds often exceeded 50% of the mean. As time progressed and hexazinone concentrations dropped, the CV increased because one watershed in the four frequently had nondetectable residue levels in runoff.

During Storm 8 (July 26, 1979) runoff carried low hexazinone concentrations from all four watersheds (20 to 45 ppbw) (Table 2). In the next significant event, Storm 10 in early September, hexazinone levels varied more. The lack of residues in watershed WS 2 stormflow reduced the mean concentration. Storm 12 produced the largest flow of the first 5 months after herbicide application, but hexazinone concentrations continued to be in the same range. Runoff from watershed WS 4 did not carry detectable levels of hexazinone during this storm. A month later, in Storm 16, hexazinone appeared in runoff from all four watersheds but at lower concentrations (1 to 15 ppbw). Storm 17 (November 2, 1979) produced the most runoff of all 26 events, but hexazinone concentrations were low. During the next two storms, watersheds WS 1 through WS 3 did not carry hexazinone residues in either runoff events. Storm 20, which occurred in mid-January, 1980, after a dry period of nearly 54 days, contained the last hexazinone residues of any size. The next three storms produced 41.4% of the

total runoff during the study but the runoff contained n[o] detectable hexazinone residues. Runoff from watershed WS [4] during Storm 24 contained the last measurable amount o[f] hexazinone (15 ppbw).

Metabolite A did not appear consistently in runoff unti[l] Storms 5 through 7 when it was detected in trace quantitie[s] (Table 2). It peaked in concentration in Storm 8, but ther[e] was present in detectable amounts in only one other runof[f] event (Storm 10). The highest metabolite A concentratio[n] was 54 ppbw in runoff from watershed WS 3 during Storm 10.

Metabolite B concentration means oscillated from nondetectable to trace levels during the first 12 storms (Table 2). Except for Storm 17, metabolite B was not detected in runof[f] after September, nearly 7 months following hexazinone application. The highest concentration in runoff from any one watershed was 15 ppbw (WS 3 following Storm 10).

Except for one water sample with a trace level (3 ppbw[)] of herbicide, residues of hexazinone and metabolites A and B were not detected in storm runoff from the untreate[d]

Table 2. Mean content of dissolved hexazinone and metabolites A and B in storm runoff from four herbicide-treated upper piedmont water sheds.

Date of storm	Storm no.	Herbicide residues[a]			Total residue runoff
			Metabolites		
		Hexazinone	A	B	
		———————(ppbw)———————			(g/ha)
1979						
April 26	1	442 ± 53	ND ± 0	ND ± 1	2.54 ± 1.25
May 10	2	105 ± 73	T(2) ± 2	T(3) ± 3	0.36 ± 0.44
May 21	3	39 ± 76	ND ± 0	ND ± 1	0.39 ± 0.74
May 31	4	107 ± 23	ND ± 0	T(6) ± 3	0.43 ± 0.32
July 8	5	11 ± 5	T(5) ± 6	ND ± 1	0.03 ± 0.05
July 12	6	T(4) ± 2	T(2) ± 4	T(1) ± 1	<0.01 ± <0.01
July 23	7	T(4) ± 5	T(2) ± 4	ND ± 0	<0.01 ± <0.01
July 26	8	34 ± 10	23 ± 18	T(2) ± 5	0.20 ± 0.20
Aug. 25	9	6 ± 12	ND ± 0	ND ± 0	0.01 ± 0.03
Sep. 3	10	30 ± 35	14 ± 27	T(4) ± 8	0.32 ± 0.35
Sep. 18	11	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
Sep. 21	12	17 ± 19	ND ± 0	T(3) ± 6	0.46 ± 0.62
Sep. 28	13	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
Oct. 4	14	T(2) ± 4	ND ± 0	ND ± 0	0.00 ± 0.00
Oct. 23	15	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
Oct. 30	16	7 ± 6	ND ± 0	ND ± 0	0.04 ± 0.02
Nov. 2	17	18 ± 10	ND ± 0	T(1) ± 2	3.02 ± 1.32
Nov. 10	18	T(4) ± 5	ND ± 0	ND ± 0	0.01 ± 0.01
Nov. 25	19	T(4) ± 4	ND ± 0	ND ± 0	0.44 ± 0.66
1980						
Jan. 18	20	14 ± 11	ND ± 0	ND ± 0	0.88 ± 0.27
March 7	21	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
March 17	22	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
March 20	23	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
March 28	24	T(4) ± 0	ND ± 0	ND ± 0	0.24 ± 0.48
April 12	25	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
May 21	26	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
					Σ = 9.39

[a]ND = <1 ppbw, and T = 1 to 10 ppbw with actual values in parentheses.

watershed WS 5. The sample with a trace level involved low flow and may have been contaminated during sample handling or analytical preparation. It did not represent a transfer of herbicide into the control watershed as subsequent samples were all negative.

Concentration models. Hexazinone and metabolite concentrations were summed by watershed for each storm and fitted to two non-linear models:

I. Power Curve:
    Concentration = a T^b,
    where   T = time in days from rainfall activation, and
            a,b = regression coefficients.
II. Maximum Concentration Estimation (30):
    Concentration = AR $(1 + 0.44 T)^{-1.6}$,
    where   A = availability for runoff index (3000 hexazinone),
                R = application rate (kg ai/ha), and
                T = time in days since the first significant rainfall after application.

The power curve model produced a significant fit to the observed data (a = 550.0; b = −1.0; F = 211.72: significance = 0.001), but overestimated the mean concentration in runoff following Storm 1 by 108 ppbw. This model also underestimated the concentrations in runoff from the next three storms. For Storm 4 onward there was reasonable agreement between observed and predicted data. Because this model reaches the non-detectable concentration levels (1 ppbw) fairly rapidly, it does not simulate the intermittent spikes and near-baseline concentrations observed 70 to 220 days after rainfall activation of the hexazinone-containing pellets.

The maximum concentration estimation model (MCE) was tested against the hexazinone residue concentrations using the 3000 availability index suggested by Wauchope and Leonard (30). The MCE prediction for peak concentration was 2812 ppbw, six-times greater than the measured value. This was somewhat higher than the four-fold overestimation proposed by Wauchope and Leonard as typical of the MCE. A non-linear regression analysis of the concentration data produced a much lower availability index (482.0) for the MCE model, but did not fit as closely as the power curve. Although it produced a better estimate of the initial storm concentration, it still suffered from the same tendency to underestimate concentrations immediately after Storm 1.

The MCE model was modified to the form:

$$\text{Concentration} = AR (1 + 0.44)^{-1.1}$$

Using this model the prediction of hexazinone residues was further improved (F = 790.32; significance = 0.001). This was especially true for data following Storms 5 through 19 in the 20- to 220-day range (Figure 2). Residue pulses were still not accounted for and concentrations in Storms 2 through 4 were again underestimated. The availability factor from the original MCE model fell to 405 with the modified model.

The residue pulses, particularly following Storms 4 and 8, which were underestimated by these models, could be due to a phenomenon discussed in greater detail in the section on soil residues. Extensive defoliation of the hardwood over-
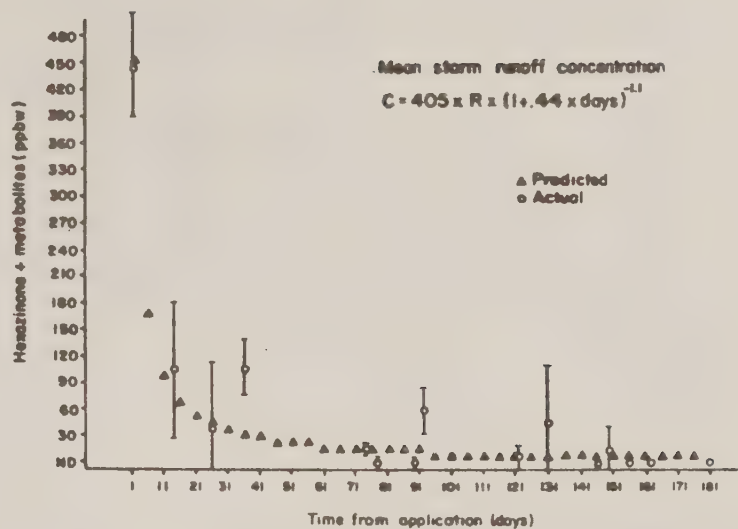

Figure 2. Modified Maximum Concentration Estimation (MCE) equation for the prediction of mean hexazinone residue concentrations in storm runoff.

story starting in late May returned significant quantities of hexazinone and its metabolites to the forest floor. This recycling could account for several of the higher-than-predicted concentrations in runoff water.

Residue outputs. Concentrations of hexazinone and both metabolites in storm runoff from each watershed were summed and multiplied by the volume of water discharge to produce a total output for each storm (Table 2). The cumulative output of dissolved herbicide residues was dominated by Storms 1 and 17 (Figure 3), which accounted for about 71% of the total herbicide loss in runoff. Storm 1 was characterized by low runoff but a high residue concentration. Storm 17 produced a very high runoff discharge, but the runoff contained only a low concentration of herbicide. By the end of Storm 26 in May, 1980, the mean output of residue in storm runoff had accumulated to 9.39 g/ha.

The source of this residue output was probably hexazinone pellets which fell in the ephemeral drainage channels. These channels, which were the source areas for storm runoff, contained 1.5% of the applied herbicide pellets. This figure was determined by flagging and counting hexazinone pellets lying in the drainage channels after application. Over the 397-day study period, the amount of hexazinone and metabolite residues lost in storm runoff was only 34.9% of that which fell into the channels, and only 0.53% of the herbicide applied on each 1-ha watershed.

The only storm which deposited any coarse sediment in the H-flumes was Storm 3. Sediment collected in the flume approaches averaged less than 400 g per watershed. The mean concentration of hexazinone plus metabolites A and B in the sediment was rather high at 250 ppbw oven-dry weight (ODW). But this amounted to an additional output of 5×10^{-5} g/ha of herbicide residue, an insignificant amount compared to that lost in the dissolved phase in the first three storms. Some organic debris, which accumulated through
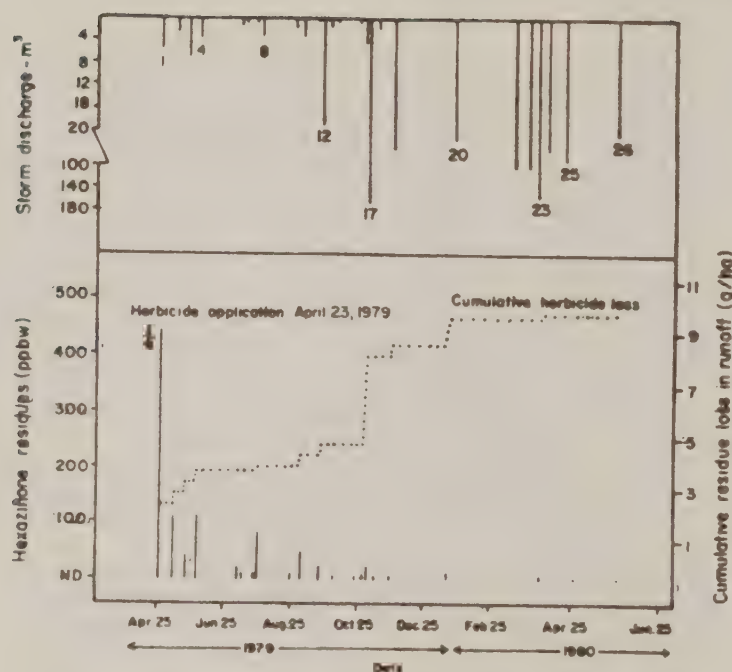
Figure 3. Mean hexazinone residues (hexazinone plus metabolites A and B) in storm runoff (vertical bars), cumulative output of residues (dots), and runoff volume (Storms 1 to 26), April 23, 1979, to May 27, 1980.

Table 3. Mean concentration of hexazinone and metabolites A and in litter and the upper 30 cm of mineral soil of watersheds trea with hexazinone April 23, 1979.

Sampling date	Time from first rain	Type of sample	Hexazinone	Metabolit A	B
			— (ppmw oven dry weight		
April 30, 1979	3	Litter	0.177	0.100	ND
		Soil	0.108	0.102	0.1
May 10, 1979	14	Litter	0.007	ND	ND
		Soil	0.043	ND	0.0
May 24, 1979	30	Litter	ND	0.103	ND
		Soil	0.063	0.015	ND
June 25, 1979	60	Litter	0.060	ND	ND
		Soil	0.015	ND	0.0
July 25, 1979	90	Litter	3.42	0.046	ND
		Soil	ND	0.025	0.0

[a]Detection limit for individual samples was <0.01 ppm. Valu listed are means of nine individual samples.

the first three storms, contained varying amounts of hexazinone (90 to 620 ppbw ODW) and metabolite A (non-detectable levels to 600 ppbw), but no detectable amounts of metabolite B. The amount of organic debris was small and was not measured.

One interesting question arises from these analyses of hexazinone and metabolite output. What would have been the impact of the largest storm (Storm 17, Figure 3) if it had occurred at the time of Storm 1? If we assume a worst-case is one in which a hypothetical Storm 1 removes the amount of herbicide Wauchope (29) classed as constituting a catastrophic loss (2%), then 160 g of hexazinone would be diluted into 172.383 m³ of runoff. This would produce a vastly greater output of hexazinone than was actually measured in the first storm. The mean concentration of runoff from this hypothetical Storm 1 (926 ppbw) would, however, be insufficient to affect aquatic algae, invertebrates, or fish (10, 19).

Soil and litter residues. Residues of hexazinone in the mineral soil, irrespective of slope position, exhibited a regular decrease over time (Table 3). The amount of metabolite residues was erratic in both litter and mineral soil. This trend paralleled that of residue concentrations in storm runoff. The half-life of hexazinone in mineral soil was in the order of 10 to 30 days. The exact half-life is difficult to determine due to the increase in concentration on May 24, 1979, relative to the previous sampling date. The mean hexazinone concentration present over the month of May would indicate a half-life of 20 days.

The increase in litter hexazinone residue measured towards

the end of June probably reflects the defoliation of the hard wood overstory. By the end of May, 1979, hexazinone ha caused almost complete necrosis of the hardwood crow (22). Leaf fall increased in June and was extensive by Jul This process apparently returned considerable amounts c herbicide to the forest floor. Data from a 1980 treatmer (Figure 4) indicates that the hexazinone content of the firs leaves shed by treated trees was less than 3.0 ppmw ODW Concentrations increased to 6.0 ppmw ODW during th
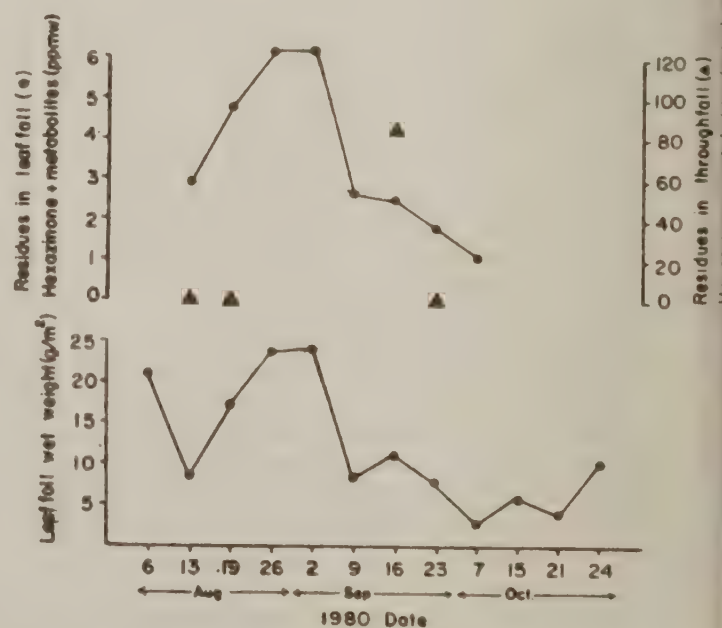

Figure 4. Hexazinone residues returned to the forest floor b litter fall and leaching after application of 1.68 kg ai/ha, 1980.

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3rd month after application, which coincided with the greatest rate of leaf deposition (240 kg/ha/week ODW). Litter data from 1979 (Table 3) indicates that hexazinone was probably the predominant residue (71 to 76%) in the 1980 leaf fall. Small amounts (12 to 157 ppbw) of hexazinone and metabolite residues were measured in 1980 in rain throughfall and litter collection gauges. These residues apparently leached out of hexazinone-affected hardwood leaves in the tree crowns and on the forest floor. Residue fluxes from affected foliage could have some effect on mineral-soil residues, but they could potentially affect herbicide concentrations in storm runoff to a greater degree. This may explain in part the elevated residue concentration following Storm 8, about 90 days after hexazinone application (Table 2). Recycling of hexazinone is consistent with the chemical properties of this herbicide, and would account for delayed herbicide activity on small hardwood stems (22). Small-diameter hardwoods, not immediately affected by the application of hexazinone pellets, did not show much herbicidal activity until the overstory crowns began to defoliate. Distribution of herbicide to these small stems may have been enhanced by return of hexazinone residues to the soil via leaf fall and subsequent leaching.

An interesting slope position-depth-time trend can be noted in the 0- to 10-cm soil residue data. Hydrologically, this is the most important depth layer in piedmont soils. It encompasses the existing A horizon developed under forested conditions and the Ap horizon remnant of past agriculture. Since the well-structured, well-drained A horizon usually overlies a massive, somewhat impervious B 2t horizon, a large proportion of subsurface water flow occurs as interflow downslope along the A-B 2t horizon boundary.

Samples from the 0- to 10-cm soil depth indicated that a pulse of hexazinone residues moved downslope during the 90 days after herbicide application (Figure 5). Residues of hexazinone and metabolites A and B peaked on the upper slopes (ridge) 3 days after the first rain, and then dropped below detection limits after 2 weeks. At the midslope position, residues also peaked on day 3 but took 30 days to drop below detection limits. At the slope toe, hexazinone and metabolite concentrations climbed steadily, peaking 60 days after the first rainfall, and dropping below detection by day 90. Further evidence to support the possibility of a downslope concentration wave moving with subsurface interflow is contained in baseflow residue data from monitoring Station No. 87.

Baseflow residues. Baseflow from the 10.4-ha watershed above the No. 87 Station averaged 0.002 m³/s during the sampling. Storm discharge reached a maximum in Storm 17 when the H-flume was overtopped by 15 cm. The discharge at maximum for the 30-cm H-flume is 0.056 m³/s. Storms 8, 10, 12, 17, and 19 through 26 produced peakflows greater than 0.011 m³/s. Except for Storms 1 through 4, which were not gauged, the remaining storms had peakflows between 0.0004 and 0.011 m³/s.

Herbicide residues were not detected in baseflow until late July, 1979 (Figure 5). The set of four residue pulses which occurred during the dry period from July 27, 1979,
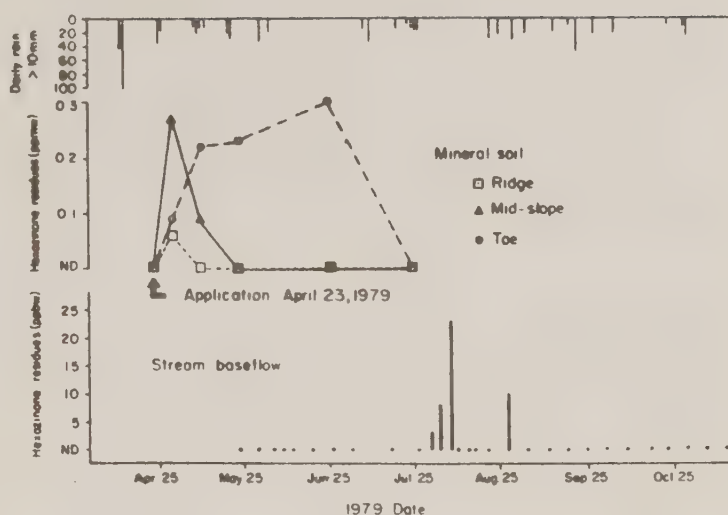
Figure 5. Hexazinone residues (hexazinone plus metabolite A and B) in the 0 to 10-cm soil depth and in baseflow in Stream A below the herbicide-treated watershed area, 1979.

to August 12, 1979, corroborate the previously discussed soil residue dynamics. These apparent pulses of herbicide residue in baseflow followed the drop in soil residue concentrations below the detection limit. The first and largest pulse peaked at 23 ppbw on August 7, 1979, but may have been higher since samples collected at Station No. 87 were instantaneous values. The second pulse is represented by a peak at about 10 ppbw. Although the sample was collected during non-storm conditions, it may have been influenced by Storm 9 on August 25, 1979. Hexazinone made up almost 49% of the first pulse and 100% of the second pulse. Metabolite A accounted for the remainder of the first pulse, but was not detected again. Metabolite B was found only in the beginning of the first residue pulse.

Samples collected manually at weekly intervals from September 4, 1979, through October 29, 1980, were generally free of herbicide residues. Individual samples on January 15, 1980, and June 24, 1980, contained trace amounts of hexazinone.

Mainstream residues. At Station No. 88, where Moonshine Creek drains a 104-ha watershed, baseflow ranged from 0.014 to 0.042 m³/s. The highest discharge was estimated at 1.7 to 2.8 m³/s.

Residues of hexazinone plus metabolites A and B in stormflow at Station No. 88 were less than 44 ppbw (Figure 6). Hexazinone was the primary residue, and metabolite B was never detected. During Storm 1, which produced the highest residue concentration in runoff from the small watersheds (442 ppbw), a trace level (2 ppbw) of hexazinone was detected in a composite sample collected automatically over a 7-day period. No residues of either metabolite were detected in this sample. Following Storms 2 and 3, no hexazinone nor metabolites were detected. A trace amount (5 ppbw) of hexazinone was detected in a 24-h composite sample after Storm 4, but again metabolites A and B were not detected.
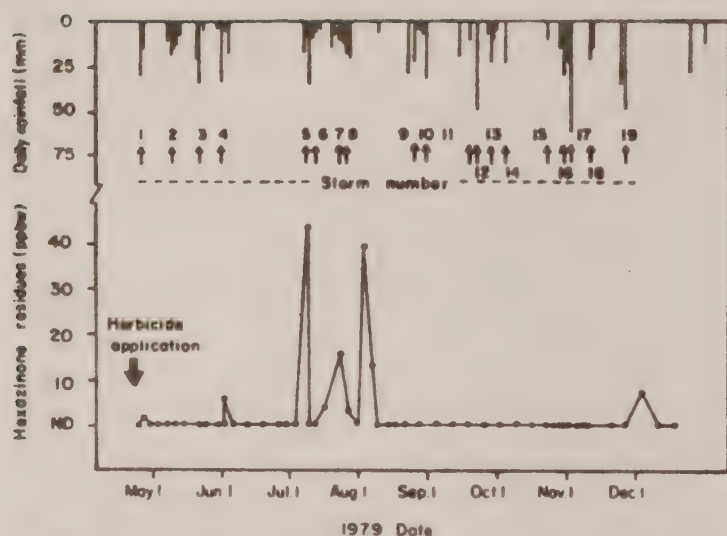
Figure 6. Hexazinone residues (hexazinone plus metabolites A and B) in solution at Moonshine Creek No. 88 gauging station, 1979.

Storm 5 in the beginning of July, 1979, was small in size (Table 1) but produced the first herbicide residue pulse of any size in Moonshine Creek (Figure 6). A manually-collected sample on July 9, 1979, contained 22 ppbw hexazinone and 21 ppbw metabolite A. Another sample taken 24 h later was free of herbicide residues. A trace amount (4 ppbw) hexazinone was detected in samples taken from Moonshine Creek between Storms 6 and 7, but neither metabolite was present. During Storm 7 which lasted from July 19 to July 24, 1979, another pulse of herbicide residue (only hexazinone) was detected in streamflow. This was followed by another trace concentration (3 ppbw of hexazinone) after Storm 8.

During the period of July 31 through August 10, 1979, another pulse of herbicide residues in streamflow occurred. The peak concentration of 40 ppbw (25 ppbw hexazinone and 15 ppbw metabolite A) occurred in a composite sample collected automatically between July 31 and August 3, 1979. The residue level fell to 13 ppbw (all hexazinone) during the next 4 days, and then returned to the non-detectable level over the next 3 days. This pulse of hexazinone residues occurred during a dry period (Figure 6) and corresponded with the pulse of residues observed in baseflow at monitoring Station No. 87.

One additional sample from Moonshine Creek in late November, 1979, contained a low level (7 ppbw) of hexazinone.

Water samples collected manually at weekly intervals from December, 1979, through October, 1980, were free of residues.

The low and intermittent concentrations of hexazinone and its metabolites in Moonshine Creek did not expose aquatic organisms to toxic herbicide levels. This conclusion was confirmed by a concurrent study of benthic organisms in Moonshine Creek (19). Aquatic invertebrates and macrophytes did not accumulate hexazinone residues, and no species composition nor diversity shifts were noted.

The application of hexazinone to forest ecosystems according to maximum recommended rates and following label instructions should not produce any adverse environmental effects on water quality or aquatic ecosystems[*].

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Impact of Hexazinone on Invertebrates after Application to Forested Watersheds

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Abstract. The impact of the herbicide, hexazinone, was assessed on aquatic macrophytes, aquatic and terrestrial invertebrate communities within forested watersheds in the Piedmont region of Georgia. Four replicate watersheds received hexazinone on April 23, 1979, and were subsequently monitored for eight months. Residue levels in terrestrial invertebrates were a maximum of two orders of magnitude greater than comparable levels (0.01 to 0.18 ppm) found in forest floor material. Aquatic organisms in a second order perennial stream were exposed to intermittent concentrations of hexazinone (6 to 44 ppb). Hexazinone and its metabolites were generally not detected (<0.1 ppm) in aquatic invertebrates and macrophytes. No major alterations in species composition or diversity were detected in the aquatic macroinvertebrate community. Terrestrial microarthropod samples collected near the end of the study period revealed no major community changes.

In the southeastern U.S., herbaceous weeds and hardwood trees are a major problem for pine silviculture. Reestablishment of harvested stands requires some form of site preparation. Current reforestation practices favor intensive mechanical systems which produce a loss of ground cover and often reduce site productivity (Brender 1973). Soil erosion is often a serious problem for years following mechanical site preparation, especially in the Piedmont, where sediment losses of 5 to 11 metric tons·ha^{-1}·yr^{-1} can occur (Nutter and Douglass 1978). Herbicides provide an alternative site preparation technique which does not contribute to erosion and have been used in the past to control hardwood competition in pine stands (Fitzgerald 1980). However, some of these chemicals have been banned because of their potential to produce adverse impacts on nontarget organisms. New compounds are being developed and tested by chemical manufacturers to meet a growing demand for herbicides that are effective, inexpensive, easy to apply, and environmentally safe. One new chemical which shows potential for forestry use in the South is hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4-($1H,3H$)-dione][2]. It is an effective herbicide on a broad spectrum of annual and perennial species. Velpar[a], with hexazinone as the active ingredient, was registered by the U.S. Environmental Protection Agency in 1975 for noncropland and right-of-way use. The pelleted formulation was granted registration for conifer release and site preparation in all states, except Alaska, California, Hawaii, Idaho, Nevada, Oregon, Utah, and Washington, in March, 1981.[3,4]

This study is part of an investigation on the loss of hexazinone in storm runoff from small forest watersheds (Neary *et al.* 1980). The objectives were: (1) to monitor accumulations of hexazinone and its metabolites in aquatic macrophytes, aquatic invertebrates, and terrestrial macroinvertebrates and (2) to determine if changes occurred in the species composition or diversity of terrestrial and aquatic invertebrate communities.

Materials and Methods

Site

The study area is in a headwater drainage of the Broad River on the Chattahoochee National Forest, Habersham County, GA.

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[2] Manufacturer E. I. duPont de Nemours, Inc., Wilmington, DE, under Trade Name Velpar[a] Gridball[a] Brushkiller. The use of trade and corporation names does not constitute endorsement by the U.S. Department of Agriculture, but is provided as a reference.

[3] This publication reports research involving pesticides. It does not contain recommendations for their use, nor does it imply that the uses discussed here have been registered. All uses of pesticides must be registered by appropriate State and/or Federal agencies before they can be recommended.

[4] CAUTION: Pesticides can be injurious to humans, domestic animals, desirable plants, and fish or wildlife—if they are not handled or applied properly. Use all pesticides selectively and carefully. Follow recommended practices for the disposal of surplus pesticides and pesticide containers.

and consists of a series of well-defined, ephemeral and first-order perennial drainages at the 400-500 m elevations. The ridgetops are broad and have been extensively eroded by past agriculture. The drainages are typically broad, bowl-shaped in their upper reaches, incised at their mid points, and broad-bottomed in their lower reaches. The valley bottoms are overlaid with extensive alluvial deposits which occasionally reach 2 m in depth. The soils are mainly Cecil sandy loam, a typic hapludult derived from gneiss and mica schist bedrock.

The study area consists of five small watersheds approximately one ha each (Figure 1). These watersheds contain similar mixed hardwood-pine stands of chestnut oak (*Quercus prinus*), white oak (*Q. alba*), black oak (*Q. velutina*), blackjack oak (*Q. marilandica*), red maple (*Acer rubrum*), sourwood (*Oxydendrum arboreum*), hickory (*Carya* spp.), and shortleaf pine (*Pinus echinata*). Four of the five watersheds, (WS-1 through WS-4) were treated with herbicide. The treatment watersheds form ephermeral drainages that merge to form a first-order perennial stream, (Stream "b"), which enters Moonshine Creek, a second-order perennial stream. Moonshine Creek watershed encompasses 104.4 ha, with most of the area forested; however the upper 10 to 15% is primarily agricultural or residential. Base-flow measured at gauge Station 88 on Moonshine Creek ranged from 14-42 l·sec^{-1} and maximum discharge measured was 776 l·sec^{-1}. The fifth watershed (WS-5) served as a control and was not treated with herbicide.

Hexazinone pellets (10% a.i.; pellet size—2 cm^3) were applied by hand to WS-1 through WS-4 on April 23, 1979 over the entire watershed, including ephemeral drainage channels, on a grid spacing of 1.2 × 1.8 m at a rate of 16.8 kg·ha^{-1}.

Rainfall was measured with a standard storage gauge and Belfort recording rain gauge located 40 m north of Watershed 5. Stream stage was measured at gauging Station No. 88 with a Belfort FW-1 water level recorder. Flow was determined by the 0.2 and 0.8 depth method using a pygmy current meter.
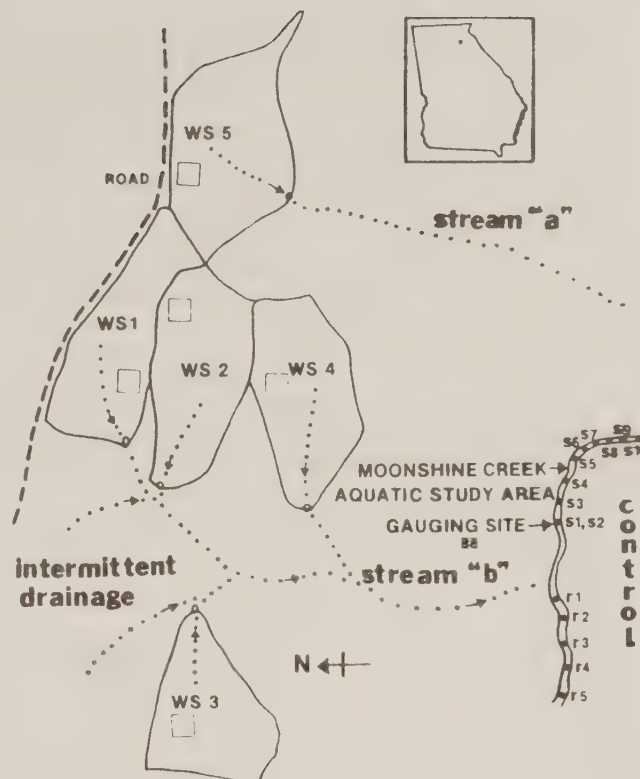

Fig. 1. Map of study areas showing treatment (WS-1 to WS-4) and control (WS-5) study sites on Moonshine Creek, Clarkesville, GA. Terrestrial invertebrate sampling plots are indicated by square (□). "R" indicates sampling locations for aquatic invertebrates and macrophytes in the stream control section and "S" indicates sample sites in the section receiving hexazinone residues

Water Sample Collection

Water samples were collected at Gauging Site 88 (Figure 1) throughout the study. The weekly bulked samples were collected by a Brailsford[4] sampler during most of the sampling period. A Manning S-4040T[5] operated from late May through June and again from late October through the end of the year. This automatic sampler collected water every two hr compositing four of these into one bottle. Grab sampling was used intermittently to supplement the automatic samplers. Water samples collected for herbicide residue analysis were placed in 1000-ml washed and methanol-rinsed jars, briefly stored at the Coweeta Hydrologic Laboratory at 4°C, transported to the University of Georgia in insulated, ice-packed containers, and stored at 4°C prior to extraction and analysis.

Forest Floor Sample Collection

Leaf litter samples were collected 3, 14, 30, 60, and 90 days after the first rain following herbicide application from areas adjacent to invertebrate collection plots. During herbicide application, in-

dividual hexazinone pellets were marked to locate individual sampling spots. Samples were collected at three equidistant points on radii of 0.6 m from each sampled pellet. Individual values for each watershed were determined from litter samples composited from samples collected from upper, mid, and lower slope areas of each of the four treated watersheds. A control sample was collected from the control watershed. Litter material was placed in labelled bags, and frozen until used for residue analysis. Studies conducted by E. I. duPont chemists indicate no loss of residues with freezer storage for up to 3 yr (Holt, personal communication).

Invertebrate and Macrophyte Collection

Macrophytes: Samples of aquatic macrophytes from rock substrate in the spray zone of the stream were collected on each date (April 1, May 12, June 16, August 17, December 1, 1979) for residue analysis. Plant material was scraped from the substrate and processed as described for stream invertebrates. Only one site per stream section (R and S) and date was sampled. Macrophytes were collected from a number of areas within each site and combined to form a representative sample for chemical analysis. Additional material was preserved in 70% ethanol for identification

Aquatic Invertebrates: Only fifteen riffle areas similar in stream flow, depth, and substrate were available for invertebrate sampling (Figure 1). Samples were collected from a large area be

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cause of the extreme heterogeneity of substrate in the riffles and its consequent effect on species distribution. A sample of at least 1 m² was necessary in order to assume the samples represent all species in the community and are from a homogeneous "parent population" (Pielou 1966a). On April 1, 1979, prior to herbicide application, samples were collected from replicate sites S-2, S-3, S-10, and R-1 to determine the adequacy of a 1 m² sample area. On May 12, 1979, samples were collected at replicate treatment sites S-4 and S-6 and at control site R-2. Samples were collected at respective treatment and control sites S-5 and R-3 on June 16, 1979, S-7 and R-4 on August 17, 1979, and S-8 and R-5 on December 15, 1979.

A "kick" sampling technique was used to collect samples. Substrate was turned by hand and invertebrates and debris allowed to float into a net with 1.6 mm mesh opening. The mesh size tended to select only the larger members of the invertebrate community. Organisms were sorted and counted in the field and stored in glass vials on ice. Upon return to the laboratory, the samples were frozen and stored at 0°C for analyses. The invertebrate samples were composited to form a single representative sample for chemical analysis per site and date. A number of representative individual specimens of each taxonomic group were preserved in 70% ethanol to determine a precise taxonomic description.

Terrestrial Invertebrates: In each watershed, a 100 m² study was established that had similar general slope, soil type, and aspect. Within each plot, individual herbicide pellets were marked with flags. On each sampling date (April 1, May 12, June 16, August 17, December 1, 1979) circular areas of 2 m² around two flags were sampled by removing the leaf litter and humus with a rake and shovel, composited for each study plot, and stored. Invertebrates were extracted from subsamples of composited leaf litter using standard Berlese funnel methods (Edwards and Fletcher 1971). Litter was stored at room temperature for about one month during subsampling and extraction.

After extraction, the macroinvertebrates were sorted, counted, and stored at 0°C prior to chemical analysis. A single representative macroinvertebrate sample was obtained by combining the entire extraction of litter subsamples for chemical analysis. No representative individuals were preserved for the determination of a precise taxonomic description of terrestrial invertebrates. In addition to macroinvertebrates, microarthropods were isolated from samples collected on August 17 and December 1, 1979, and preserved in 70% ethanol.

Community Evaluations: A diversity value for each aquatic invertebrate sample was calculated by an index based on information theory derived from the Shannon formula (Shannon and Weaver 1963). Wilhm and Dorris (1968); Wilhm (1970a), and Bradt (1978) have used this index to quantify the diversity of aquatic macroinvertebrate communities. A coefficient of community value was calculated for each sample using an index presented by McIntosh (1967) and Whittaker (1975). This index has been used in determining similarity among communities in various ecosystems including aquatic systems containing benthic macroinvertebrates (Burlington 1962). Values may range from 0, indicating perfect dissimilarity, to 1, indicating perfect similarity.

Extraction and Analysis of Hexazinone

Analysis for hexazinone and its metabolites (A, B, D, and E) utilized a modification of a method by Holt (1981). A 25-g sample of the total invertebrate or macrophyte sample was weighed into a Waring® blender and 120 ml of chloroform added together with

50 g of sodium sulfate (Na₂SO₄). Each sample was blended at high speed for about 5 min, and vacuum filtered through Whatman glass filter paper in a Büchner funnel. The chloroform extraction was repeated twice using additional 100 ml portions of solvent. Finally, the sample was blended for 5 min with 150 ml of ethyl acetate and the homogenate was filtered. The combined extracts were filtered through double glass filter papers with 50 g Na₂SO₄ on the filter. The combined filtrates were quantitatively transferred to a 1000-ml round-bottom flask. Water (75ml) was added to the combined extracts and the organic solvents were removed with a rotary evaporator at 60°C. The remaining water was transferred through a glass wool filter to a 250 ml separatory funnel with small volumes of water as rinse. The flask was rinsed with chloroform and methanol until clean and then rinsed with water. Hexane (50 ml) was added to the separatory funnel. The funnel was shaken gently for about one min, and the phases allowed to separate. The water layer was run back into the 1000-ml round-bottom flask, discarding the hexane. The hexane wash was repeated twice with 50 ml portions of solvent and the sample was rinsed back into the separatory funnel each time with water. After the last hexane wash, the 1000-ml round-bottom flask was rinsed with methanol several times and finally with chloroform. Chloroform (75 ml) was added to the aqueous phase in the separatory funnel and shaken for 2 min. The phases were allowed to separate, and the chloroform was filtered through glass wool and Na₂SO₄ into the 100 ml round-bottom flask. The chloroform extraction was repeated twice with additional 75 ml portions of solvent. The volume was reduced to 4 ml on a rotary evaporator and transferred to a 10-ml culture tube with several chloroform/ethyl acetate rinses. The samples were stored in a freezer for future analysis.

At the time of analysis, extracts were concentrated to dryness in a water bath at 60°C under a stream of nitrogen. The residue was dissolved in one ml of chloroform and the sample reacted with trifluoroacetic anhydride. The derivatives were analyzed by gas-liquid chromatography on the same day as derivitization with a Tracor Model 222 Gas Chromatograph equipped with a Tracor Model 702 N/P detector. The chromatographic column was 15% OV-17 on 100/120 Chromosorb W HP (Supelco, Inc., Bellefonte, PA); 914 mm glass, 6.35 mm O.D., 1.59 mm I.D. The gas chromatograph operating conditions were: Inlet temperature, 230°C; detector temperature, 280°C; helium carrier gas flow, 35 ml/min. The column was temperature-programmed from 230° to 280° C at a rate of 10°/min. The column was held at the final temperature for about 8 min. Hexazinone and metabolite levels were determined by comparison of peak height in sample chromatograms to those of an analytical standard. All reference standards of hexazinone and metabolites A, B, D, and E were obtained from the Biochemicals Department, Agrichemicals Marketing Division, E. I. duPont de Nemours & Co., Inc., Wilmington, DE. A reagent blank and a spiked sample were included with each set of analyses, and values were corrected for percent recovery.

Results

Water Sample Residues

The residues of hexazinone and metabolite (hexazinone plus metabolites A and B) detected at Gauging Site 88 and monthly rainfall are presented in Figure 2. Metabolite B was never detected in streamflow at the 88 site. For much of the experi-
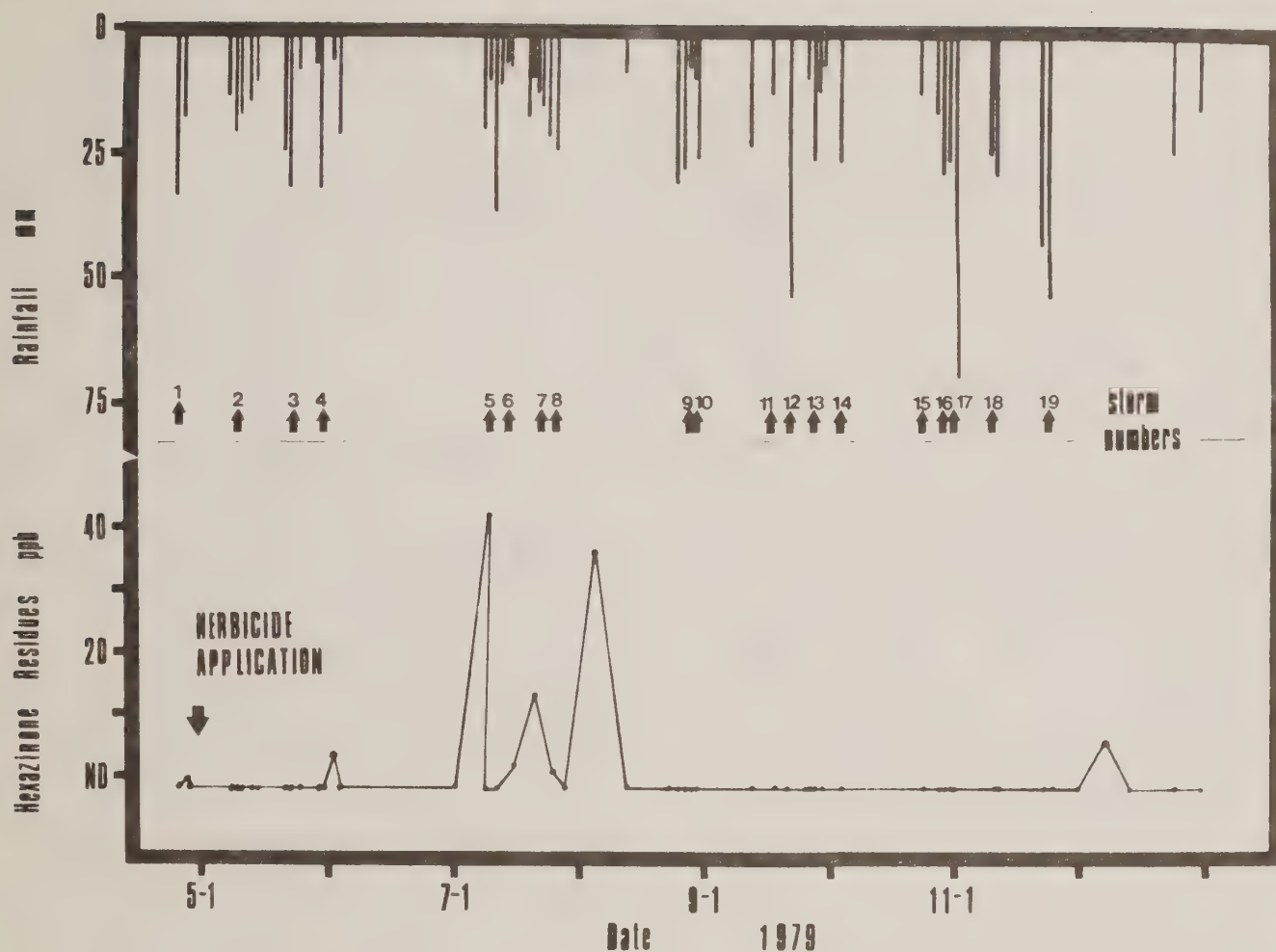
Fig. 2. Hexazinone residue (hexazinone plus metabolite A and B) in solution at Moonshine Creek Gauging Site No. 88

mental period, levels were below the 1 ppb analytical detection limit. Detectable concentrations (6 to 44 ppb) occurred during July and early August. Residues of metabolite A first appeared in the peak of July 9, 1979, contributing nearly one-half of the total residue concentration. The August 8th peak, which was not associated with a storm was composed of 62% hexazinone and 38% metabolite A (not detected again at Gauging Site 88). Peak residue levels did not show any direct relationship to the magnitude of storm events nor did periods of elevated concentrations coincide with all storm events. Hexazinone residues were detected only during storms 1, 4, 5, 7, and 8. The residue peaks were short in duration, and low in concentration.

Forest Floor Residues

Samples of the forest floor, litter and decomposed humus material lying above the mineral soil, contained residues of hexazinone for up to 90 days following the first rain after herbicide application (Table 1). Residues of metabolite A were present three days after the first rainfall but were not detected thereafter. Metabolite B was not detected in the forest floor material. Since samples were collected at a maximum distance from application points, these concentrations are minimum levels of exposure for terrestrial invertebrates in the forest floor.

Hexazinone and Metabolite Residue in Organisms

Residue levels of hexazinone and its metabolites above the limit of analytical detection (0.1 ppm) were observed in aquatic macrophytes (composed primarily of aquatic mosses *Ecrhynchium rusciforme* and *Leptodictyum riparium*) and macroinvertebrates on only a few occasions. Macroinvertebrates collected on May 12, 1979, from S-4 and S-6 exhibited respectively a trace of metabolite B and 0.24 ppm (wet weight) metabolite D. A trace of metabolite B was again encountered in a macroinvertebrate sample collected on December 15,

Table 1. Residues of hexazinone and metabolites A and B in forest floor material. Moonshine Creek study area. 1979

Sample date 1979	Days from first rainfall	Herbicide residue[a]		
			Metabolites	
		Hexazinone	A (ppm, oven dry weight)	B
4/30/79	5	0.18 ± 0.19	0.10 ± 0.17	ND[b] —
5/10/79	15	0.01 ± 0.01	N.D. —	ND —
5/24/79	29	N.D. —	0.16 ± 0.22	ND —
6/25/79	61	0.07 ± 0.10	N.D. —	ND —
7/25/79	91	0.06 ± 0.06	N.D. —	ND —

[a] Values are means determined for replicate watersheds (WS-1 to WS-4, inclusive) ± 1 standard deviation
[b] Limit of analytical detection of 0.01 ppm; for purposes of mean concentrations of hexazinone, a value of 0.01 was used for nondetectable (ND) residues. Due to the presence of interfering substances and small sample size. metabolites D and E were not reported

1979, from S-8. Also, trace amounts of compounds similar to metabolites E and D were observed respectively on March 31 and June 16, 1979, in macrophytes from the control section suggesting that interfering substances, chemicals similar to hexazinone's metabolites, are present in the aquatic environment.

Most soil macroinvertebrate samples showed detectable concentrations of hexazinone and/or its metabolites. However, the values from replicate watersheds on any one sampling date proved to be highly variable (Table 2). This variability probably resulted from the small, heterogenous samples of invertebrates and the variation in microhabitats between replicate watersheds. As in aquatic samples, unidentified interfering substances are present as evidenced by the detection of these substances in samples from the control watershed.

Community Composition

I. Aquatic Macroinvertebrates

Samples from 1 m² proved to be adequate for diversity estimates. The diversity values for 1 m² samples collected on April 1, 1979, were within 10% of the asymptotic diversity as estimated by the pooling of samples (Pielou 1966b). Similar variations in diversity with time were noted for hexazinone receiving and control sections of stream (Figure 3). With the assumption of no interaction between time and treatment effects supported by the similar variations in diversity with time for each stream section, an analysis of variance without replication was used with collection dates as random effects and hexazinone receiving and control sections as fixed treatment effects (Sokal and Rohlf 1969). Dates May 12 through December 15, 1979, were included in the analysis. No significant differences were noted between hexazinone receiving and control sections at the 0.10 level, $F = 1.30 < 4.54$. The

coefficient of community values were assembled into a similarity matrix for each sampling date (Table 3). Values equal to or greater than 0.65 were considered to indicate ecological similarity by Beckett (1978), Hurd (1961), and Hanson (1955). All values in this study were equal to or greater than 0.65 indicating marked similarity between the control section and the section of the stream receiving hexazinone residues. Apparently, the residues had little effect on the composition of the aquatic macroinvertebrate community.

As a measure of the abundance of a taxon in the control and treated sections, the numbers of individuals of a specific taxon per sample were expressed as a percentage of the total number of aquatic invertebrates collected per sample. Only taxa that composed 10 percent or more of a minimum of one sample were compared graphically (Figures 4 and 5). Taxa present in samples in percentages of less than 10% were found in samples only sporadically and consequently did not provide meaningful information on the effects of hexazinone on their appearance in the community. The taxa compared in samples collected from both stream sections showed similar temporal variations in abundance throughout the sampling period. There is no evidence that hexazinone altered taxa abundance.

II. Terrestrial Invertebrates

Terrestrial macroinvertebrate samples were too small to derive meaningful information regarding the effects of hexazinone on community composition. The diversity values of pooled replicate samples indicated that sample size was not adequate for diversity and similarity studies (Pielou 1966b; Wilhm 1970b). The only observation that may be of significance occurred in samples collected on August 17, 1979, when at least twice the number of

Table 2. Concentration means and ranges of hexazinone and metabolites A and B in terrestrial invertebrate samples from treated and untreated watersheds, Moonshine Creek study area, 1979

| Date | | ppm[a] | | | | | |
| | | Hexazinone[b] | | met. A | | met. B | |
		Level	Range	Level	Range	Level	Range
3/31/79	Before application	ND		ND		ND	
5/12/79	Control	ND		ND		0.67	
	Treated	0.35	ND–1.34	ND		0.43	ND–0.95
6/16/79	Control	ND		ND		ND	
	Treated	0.13	ND–0.50	0.97	ND–3.88	0.74	ND–1.72
8/17/79	Control	ND		ND		ND	
	Treated	ND		ND		1.43	ND–4.29
12/1/79	Treated	ND		ND		ND	

[a] Ppm is determined on an "as is" basis. Values for the control watershed WS-5 were determined from a single sample. Values for 12/1/79 were from a single sample from watershed WS-4. Means and range were determined from samples collected from watersheds WS-1 to WS-4. ND is interpreted as zero for calculation of means
[b] Due to the presence of interfering substances and small sample size, Metabolites D and E were not reported. Presence of hexazinone in Control 5/12/79 sample probably indicates interference in the analytical procedure
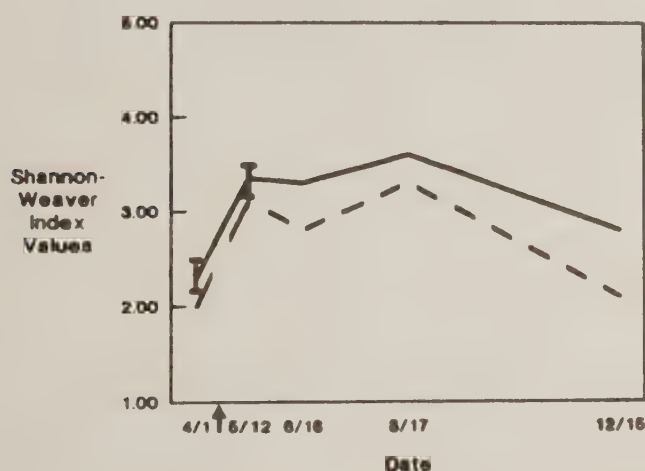

Fig. 3. Shannon-Weaver Index values calculated for aquatic invertebrates in treated and control sections of Moonshine Creek, 1979. Error bars indicate the range of values for a mean of replicate samples. Values without error bars were determined from a single sample. (——— treated area, – – – control, ↑ date of hexazinone application)

Table 3. Similarity matrices for the coefficient of community index calculated for sites receiving hexazinone residues and control sites, Moonshine Creek, 1979

April 1	Sites[a]	S-2	S-3	S-10	R-1
	S-2	1	0.92	0.88	0.88
	S-3		1	0.80	0.80
	S-10			1	0.85
	R-1				1
May 12	Sites	S-4	S-6	R-2	
	S-4	1	0.69	0.65	
	S-6		1	0.86	
	R-2			1	
June 16	Sites	S-5	R-3		
	S-5	1	0.79		
	R-3		1		
August 17	Sites	S-7	R-4		
	S-7	1	0.88		
	R-4		1		
December 15	Sites	S-8	R-5		
	S-8	1	0.65		
	R-5		1		

[a] Sites designated with "S" indicate sites below the entry point of hexazinone into the stream; sites designated with "R" indicate sites above the entry point of hexazinone

individuals were collected in the control watershed (WS-5) compared to the number collected in any one herbicide treated watershed (WS-1 to WS-4, inclusive).

The variation in soil microarthropod numbers in samples from treated watersheds was large, suggesting that microhabitat differences exist within watersheds. Since microarthropods were not identified below family, the number of taxa per sample was consistently less than that needed for a meaningful calculation of the Shannon-Weaver Index or Coefficient of Community Index. Therefore, the abundance of a specific taxon was expressed as a percentage of the total number of individuals collected per sample. Only those taxa that composed 5% or more of a minimum of one sample were compared tabularly (Table 4). Acarina composed a large fraction of the microarthropod community in all watersheds, and its abundance did not vary appreciably between control (WS-5) and herbicide treated watersheds (WS-1 to WS-4, inclusive). The remaining taxa also showed no consistent variation between herbicide treated and control watersheds.
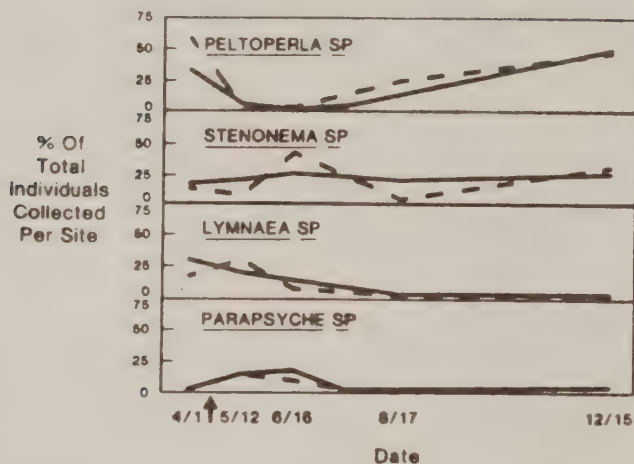
Fig. 4. Percent of the total number of individuals per site for 4 major taxa (*Peltoperla* sp., *Stenonema* sp., *Lymnaea* sp., and *Parapsyche* sp.) collected from Moonshine Creek, 1979. (——— treated area, – – – control, ↑ date of hexazinone application)
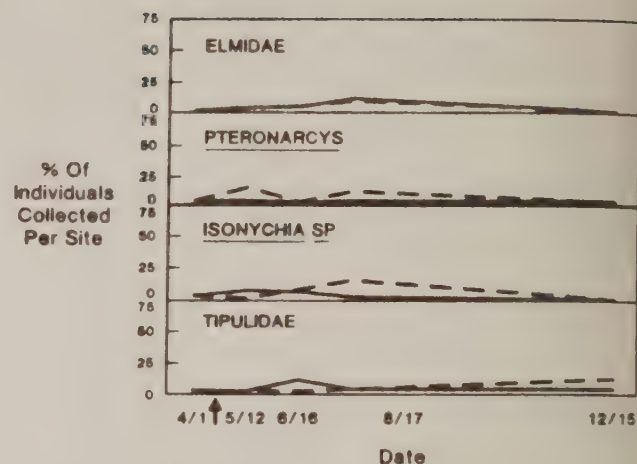
Fig. 5. Percent of the total number of individuals per site for four major taxa (Elmidae, *Pteronarcys dorsata, Isonychia* sp., Tipulidae) collected from Moonshine Creek, 1979. (——— treated area, – – – control, ↑ date of hexazinone application)

Table 4. Abundance of taxa as a percentage of the total number of microarthropods in a sample, and the total number of individuals and taxa in samples from treated and untreated watersheds, Moonshine Creek study area, 1979

| Order | Organisms[a] | August 17 sites | | | | |
		WS-1	WS-2	WS-3	WS-4	WS-5
Hymenoptera	Formicidae	1.6	0.0	0.6	0.2	2.1
Acarina		60.8	83.5	89.5	89.4	88.1
Araneae		5.8	5.0	1.1	1.5	1.3
Collembola		19.0	0.3	0.6	3.6	1.4
Psocoptera		0.0	5.9	0.2	0.0	0.0
Total per sample		189	661	2879	1826	1573
Taxa per sample		14	10	16	12	15
		December 1 sites				
		WS-1	WS-2	WS-3	WS-4	WS-5
Hymenoptera	Formicidae	8.3	17.5	0.0	10.5	6.8
Acarina		58.3	68.2	71.0	62.0	69.9
Araneae		4.2	1.6	1.3	4.4	2.7
Collembola		25.0	4.8	19.7	19.6	15.1
Psocoptera		0.0	0.0	0.8	0.0	1.4
Total per sample		24	63	238	229	73
Taxa per sample		5	6	8	9	8

[a] Organisms could not be identified to a lower taxonomic unit as a result of the lack of late instar specimens. Only those taxa that composed 5% or more of any one sample were tabulated. The remaining taxa composed less than 5% of any one sample on each sampling date

Discussion

Mainstream Residues

Mainstream residue levels for hexazinone plus its metabolites were low (<44 ppb), because of the small loss of hexazinone from the treated watersheds and dilution downstream. The effect of mainstream dilution during storm discharge is considerable; during Storm 1, which produced the highest average residue concentrations of 442 ppb from the small watersheds (Neary *et al.* 1980), only 1.5 ppb hexazinone was detected in a 7-day bulk sample. Losses of herbicide residues were episodic and unpredictable. They occurred as pulses of short duration during most of the study period, and did not coincide with peak storm runoff, but occurred several days later. This suggests that other mechanisms, such as subsurface flow, may be the dominating factors in the loss of residues. As a consequence, aquatic organisms were exposed inter-

mittently to short duration, low-level concentrations of hexazinone residues over a period of 8 months. The concentrations of hexazinone residues to which aquatic organisms were subjected in this study are typical of anticipated uses of hexazinone as a forest herbicide where <5% of a second-order watershed is treated. The degree of streamflow dilution is dependent upon the relative sizes of treated and untreated areas of the watershed. The maximum concentration of herbicide residues to which aquatic organisms would be exposed would occur only where the entire drainage area of a perennial stream, such as Stream "b", was treated with hexazinone. In this study, the maximum measurement was 442 ppb (Neary *et al.* 1980).

Forest Litter Residues

Hexazinone residues in the forest litter were much higher than mainstream residues. Residues were mainly the parent compound (0.01 to 0.18 ppm). Attenuation of hexazinone concentrations is likely to follow normal residue decay curves. Since no forest litter samples were collected from August to December, no comparisons of levels of hexazinone in the forest litter and terrestrial invertebrates can be made.

Accumulation of Hexazinone in Organisms

Hexazinone residues in mainstream flow did not reach levels shown to affect aquatic organisms in laboratory studies nor was there any evidence that hexazinone accumulated in stream organisms. Fowler (1977) has shown in the laboratory that the common algae *Cladophora clomerata*, *Rhizochonium hieroglyphium* and *Vaucheria dichotoma* are inhibited at 0.5, 0.5, and 1.0 ppm, respectively. *Daphnia* sp., a freshwater invertebrate, has an LC_{50} (48 hr) of 151 ppm and, in a 21-day life cycle study, the effective concentrations for an LC_{50} with 7- and 3-day renewal of hexazinone were 33.1 and 20 to 50 ppm, respectively (Summers, personal communication). In this study stream, organisms were exposed for periods of 1 to 10 days to detectable concentrations of hexazinone that were one to four orders of magnitude less than the effective concentrations in laboratory studies. Although stream organisms were intermittently exposed to detectable herbicide residues throughout the study period, the accumulation of residues, if any, in organisms was less than one order of magnitude above the maximum concentration observed in Moonshine Creek. Notwithstanding, there is limited information regarding the impact of hexazinone on stream organisms.

In contrast to the aquatic biota, hexazinone and its metabolites accumulated in terrestrial macroinvertebrates. Mean levels of hexazinone or at least one of its metabolites were one to two orders of magnitude greater than comparable levels found in forest litter. This suggests a significant uptake of hexazinone by the macroinvertebrate community, either by active biological uptake or passive accumulation. Since invertebrate levels were determined on a wet weight basis and levels in the forest litter were determined on a dry weight basis, the actual differences in invertebrate and forest litter hexazinone levels are somewhat greater than indicated by the data. More information on the mechanism of uptake and the concentrations which impair the function of, or kill, invertebrate organisms would be needed to evaluate the significance of the observed accumulations of terrestrial macroinvertebrates.

Community Composition

The marked similarity in diversity and species composition exhibited between control and herbicide treated sections of stream indicate that no gross changes in the aquatic invertebrate community occurred as a result of the introduction of hexazinone residues into the aquatic environment. No large or consistent variations in the abundance of major taxa of soil microarthropods were observed between control and herbicide treated watersheds. Nevertheless, information on the effects of the herbicide treatment on terrestrial and aquatic invertebrate communities is limited. Reduced sample replication, large variation between replicate samples, incomplete taxonomic description of samples and a sampling schedule of less than one year can mask subtle effects. Diversity values at all stream sites on all sampling dates were somewhat lower than expected. Diversity values equal to or greater than 3.0 are indicative of "clean" water and are expected to range from 3.0 to 4.0 for small mountain streams (Wilhm 1970a). Only samples collected in the summer fell into this category. The low values may be the result of incomplete taxonomic description (*i.e.*, the lack of separation of species present in higher taxonomic units) and/or the lack of complete sampling (*i.e.*, sandy areas in pools), or the result of other perturbations of the stream from farmland, roads, and a railroad right-of-way occurring upstream of the study area.

Bormann and Likens (1979) demonstrated that devegetation of a forested ecosystem disrupts the regulation of hydrologic, energy flow, decomposition, mineralization, erosion, and nutrient cycling processes. The disruption of regulation of these

processes would probably also alter the abundance of invertebrates and the organization of aquatic and terrestrial invertebrate communities within the ecosystem. The removal of vegetation rather than herbicide toxicity is probably responsible for the decrease in the abundance of macroinvertebrates during the later summer months. The increased heat and light reaching the forest litter most likely forced the invertebrates into the mineral soil. The impacts of devegetation on ecosystem processes often occur several years later; therefore, the full impact of hexazinone application on invertebrate communities may not be evident in this study. The extent that devegetation will disrupt steady-state regulation, and consequently invertebrate communities, will depend upon the extent of devegetation and the rate and type of revegetation that consequently restores biotic regulation. Methods for separating indirect and long-term effects of vegetation removal from direct toxic effects of hexazinone are needed to more thoroughly assess the impact of hexazinone on the invertebrate communities of forested ecosystems.

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WATER QUALITY OF EPHEMERAL FOREST STREAMS AFTER SITE PREPARATION WITH THE HERBICIDE HEXAZINONE

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ABSTRACT

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Four small watersheds (1 ha) in the upper Piedmont of north Georgia were treated with 1.68 kg ha^{-1} active ingredient of hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione] pellets. Residues in stormflow peaked in the first storm (442 mg m^{-3}), declined rapidly thereafter, and disappeared within 7 months. Loss of hexazinone in stormflow averaged 0.53% of the applied herbicide. Suspended solids concentrations in runoff from the treated watersheds averaged 50.4 ± 7.9 g m^{-3} and were slightly more than those of the control (36.4 ± 5.4 g m^{-3}). Total sediment yields were increased by a factor of 2.5 due to increased runoff associated with site preparation using herbicide and salvage logging. However, sediment loadings remained below those produced by mechanical techniques and well within levels common in relatively undisturbed forests. Hexazinone treatment produced a large increase in NO_3-N concentrations (peak of 5328 mg m^{-3}), but NO_3-N levels returned to normal within 2 years. Data indicate that hexazinone may have produced some stimulation of nitrifying bacteria. Cation concentrations increased 30—100% as a result of hexazinone application, but these increases were also transient. Overall, water quality changes were small and short-lived.

INTRODUCTION

Mechanical site preparation improves regeneration success but raises concerns about accelerated erosion losses (Ursic and Douglass, 1978; Beasley, 1979; Douglass and Goodwin, 1980). Recent legislation has called attention to intensive forestry as sources of nonpoint source pollution.

Variable effects on water quality have been documented (Beasley, 1979; Hewlett, 1979; Douglass and Goodwin, 1980; Fisher, 1981; Riekerk, 1982). Prescribed burning has been a successful alternative for reducing competition in regenerating stands with minor water quality impacts (Ursic, 1970;

Cushwa et al., 1971; Lewis, 1974; Richter et al., 1982; Douglass and Van Lear, 1983). Little information is available on water quality impacts of yet another site preparation alternative: herbicides.

Hexazinone* is a symmetrical triazine herbicide which is effective in controlling a broad spectrum of annual and perennial weeds at rates tolerated by many conifers. Both clay pellets and liquid formulations have considerable potential to be cost—effective and environmentally compatible tools in pine silviculture (Hamilton, 1979; Gonzalez, 1980; Michael, 1980; Neary et al., 1981, 1983; Mayack et al., 1982).

The objective of this paper is to evaluate the nonpoint source pollution potential of the herbicide hexazinone by (1) briefly summarizing previously-published findings on offsite movement; (2) evaluating erosional losses, and (3) evaluating changes in the anion and cation content of stormflow and some of the in situ processes which might affect their concentrations.

MATERIALS AND METHODS

Site description

The study site is located in the Chattahoochee National Forest in northeast Georgia, at 400 to 450 m elevation (Fig. 1). First-order watersheds are typically broad, bowl-shaped in their upper reaches, deeply eroded at their midpoints, and broad-bottomed in their lower reaches. The original first-order perennial channels and valley bottoms are buried under 1—2 m of fine-textured, alluvial deposits. Moonshine Creek, a second-order perennial stream, alternates from low gradient sections with sandy bottoms to steep ones with rocky riffles, pools, and waterfalls. Baseflows range from 0.01 to 0.05 m^3 s^{-1}. Yearly precipitation averages 1300—1400 mm with autumn and winter frontal storms and summer thunderstorms.

Soils are well-drained sandy loams of the Cecil series (clayey, kaolinitic, thermic Typic Hapludults) formed from mica-rich gneiss and schist of the pre-Cambrian Tallulah Falls formation. They are acid (pH 4.5 to 5.5), moderately permeable (50—300 mm h^{-1}), and contain up to 1.6% organic carbon in the upper 0.6 m. Upper ridges contain eroded phases of the Cecil series with a remnant A horizon (0—0.10 m thick) overlying an eroded Bt horizon. The A horizon increases in thickness on the toeslope. Bottomlands surrounding the headwaters of perennial streams are colluvial in nature.

Predominant vegetation was a 60—80-year-old mixed pine—hardwood association characterized by scattered shortleaf pine (*Pinus echinata* Mill.),

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*Manufactured by E.I. DuPont de Nemours and Company, Inc., Wilmington, DE, as Velpar L® and Velpar 90, and previously as Velpar® Gridball® Brushkiller. Also distributed by Proserve, Inc., Memphis, TN, as Pronone®. The use of trade and corporation names throughout the manuscript does not constitute endorsement by USDA but is provided as a reference.

chestnut oak (*Quercus prinus* L.), white oak (*Q. alba* L.), black oak (*Q. velutina* Lam.), flowering dogwood (*Cornus florida* L.), sourwood (*Oxydendrum arboreum* (L.) DC), pignut hickory (*Carya glabra* (Mill.) Sweet), and various other species (Neary et al., 1981). The sparse understory consisted of overstory hardwood species and various herbaceous plants.
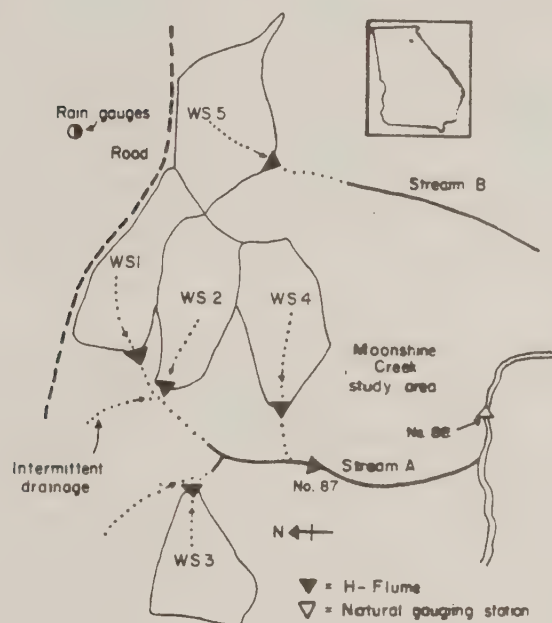

Fig. 1. Watershed and H-flume locations, hexazinone study area, Moonshine Creek, Chattahoochee National Forest, GA. Watershed 1, 2, 3, and 4 received 1.68 kg active ingredient ha^{-1} hexazinone; watershed 5 served as control.

Instrumentation

Five ephemeral watersheds (WS 1 to WS 5), 0.85—1.09 ha in area, were selected and surveyed in early March 1979 (Fig. 1). They were instrumented in April 1979 with recording rain gauges (Belfort standard weighing-bucket recording rain gauge equipped with clock drive and 96-h gears, Belfort Instrument Company, Baltimore, MD) 0.3-m H-flumes, Coshocton wheel flow-proportional samplers, analog water-level recorders (Analog FW-1 water level recorders equipped with clock drive and 96-h gears, Belfort Instrument Company, Baltimore, MD), and sample collection systems (Brakensiek et al., 1979). Cutoff walls for the H-flumes were entrenched into an indurated Bt horizon and cemented in place to contain all surface flow. The flow-proportional samplers were designed to collect approximately 0.5% of total stormflow (Neary et al., 1983).

Watersheds 1—4 were selected for herbicide treatment because surface runoff from these watersheds converges into the same first-order channel

(Stream A, Fig. 1). Over much of its length, this small, first-order perennial stream alternates from open channel flow to subsurface flow in recent alluvium.

Treatment

Watersheds 1—4 plus some surrounding areas were treated with 1.68 kg ha⁻¹ of hexazinone (10% active ingredient pellets) on 23 April 1979. The pellets were manually applied on a grid of 1.2×1.8 m. Eight months after the herbicide application, WS 1, 2, and 4 were logged to remove mature shortleaf pine and then opened up to firewood logging. Some minor disturbance to the forest floor resulted from operation of rubber-tired skidders. Watershed 3 was not disturbed by any logging activities.

Water and sediment sampling

Runoff samples were collected during each storm between 16 April 1979 and 7 April 1981. Samples for hexazinone analysis were processed by standard techniques and shipped to University of Georgia for analysis (Neary et al., 1983). Hexazinone residues were extracted and analyzed to a detection level of 1 mg m⁻³ by standard techniques and gas chromatography using a method developed by Holt (1981). Aliquots of the storm runoff were placed in duplicate 250-ml polypropylene bottles and transported to the Coweeta Hydrologic Laboratory (Otto, NC) for analysis. Suspended solids were determined gravimetrically by filtering 50—250 ml of sample through a 0.42×10^{-6} m fiberglass filter and then drying at 105°C. Solution cations, calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), and sodium (Na^+) were measured by standard atomic absorption spectroscopy (Perkin-Elmer Model 305 atomic absorption spectrophotometer; Perkin-Elmer Corp., Norwalk, CN). Nitrate nitrogen (NO_3-N), ammonium nitrogen (NH_4-N), chloride (Cl^-), orthophosphate (PO_4^{3-}), and sulfate (SO_4^{2-}) were determined to a level of 1 mg m⁻³ by standard automated colorimetric methods (McSwain, 1973) (Technicon Autoanalyzer II equipped with sampler, pump, colorimeters, chart, and digital output; Technicon, Inc., Terrytown, NY). Water quality parameters were compared for statistically-significant differences between the control and treated watersheds using paired t-tests.

The hexazinone content was determined for each of 26 stormflow events from 16 April 1979 to 27 May 1980. Anion and cation concentrations were measured on a storm-by-storm basis from 16 April 1979 until 31 May 1979 (four storms). Samples were composited monthly on a stormflow-volume basis for the next 8 months due to problems with laboratory analytical loads. From March 1980 through 7 April 1981, only major storms were sampled and analyzed. Suspended solid concentrations were measured on all runoff samples from 16 April 1979 through 7 April 1981.

Microbiological processes

Soil samples were collected from the upper 0.1 m in each treated watershed and stored in sealed plastic bags at 4°C. Samples (1.3 g) were placed in 120-ml glass bottles and supplemented with 30 ml sterile, degassed water, 10 mM nitrate, and 5.5 mM glucose. Commercial-grade hexazinone was added to the soil slurries to provide concentrations of 10 and 100 mg kg⁻¹ active ingredient. Data from Neary et al. (1983) showed that interpellet concentrations were 0.1 mg kg⁻¹ and calculations indicated that concentrations immediately under the pellet would be 150 mg kg⁻¹. Thus, two intermediate rates were selected. The slurries were mixed, sparged for 5 min with oxygen-free helium, and then sealed with serum bottle stoppers. Acetylene (1% v/v) was added to the headspace. Gas production by these slurries was monitored by gas chromatography (Grant and Payne, 1981) (Carle Model III Analytical Gas Chromatograph fitted with a Poropak Q Column, 304 cm by 0.32 cm, and a molecular sieve 5A column, 100 cm by 0.32 cm, both operated at 50°C).

The denitrifier *Pseudomonas fluorescens* was grown at 30°C in sealed, 120-ml bottles containing trypticase soy broth plus 0.2% NaNO₃ under a helium plus 1% acetylene atmosphere. Gas production by this species was also monitored by gas chromatography. The nitrifier *Nitrobacter winogradskyi* was grown in the medium of Schmidt et al. (1973) supplemented with a 0.5% soil extract. Cultures were incubated at 30°C on a 200-rpm rotary shaker. *Nitrosomonas europaea*, another nitrifier, was grown in the medium of Alexander and Clark (1965) on a 200-rpm rotary shaker at 30°C.

Total cell numbers of *Nitrobacter winogradskyi* and *Nitrosomonas europaea* were determined using a Petroff—Hauser counting chamber and phase contrast microscope. A solution of hexazinone was filter sterilized and added to the bacterial cultures at final concentrations of 10 and 100 mg kg⁻¹ active ingredient. Nitrate was analyzed by the technique of Strickland and Parsons (1968).

Denitrifier population levels in soil samples from the study site were measured using a MPN technique described by Tiedje (1982).

RESULTS AND DISCUSSION

Precipitation and storm runoff

Rainfall during 1979 set new records, with an excess of 30% above the 1350 mm average (Neary et al., 1983). It remained wet through May 1980, with precipitation 31% above average due to record rainfall in March (441 mm, 162% of average). From late June through the remainder of 1980 and into the first half of 1981, rainfall was near record low (60% of normal for the 12-month period of July 1980—July 1981). Nine storms during the 784-day period of the study accounted for 84% of the total stormflow.

TABLE 1

Suspended sediment concentrations and total output in storm runoff from herbicide-treated watersheds in the upper Piedmont, 1979–1981

Watershed treatment	Observations	Suspended sediment Concentrations (g m⁻³) Mean ± S.E.	Minimum	Maximum	Output Total (kg ha⁻¹)	1st year (kg ha⁻¹ year⁻¹)	Stormflow volume (m³)
1 Herbicide and salvage log	44	28.0 ± 4.6	2.5	161.1	110.6	107.3	1617.3
2 Herbicide and salvage log	44	48.4 ± 16.0	2.2	675.8	87.0	84.4	1102.6
3 Herbicide	45	61.6 ± 22.3	2.4	980.8	108.4	105.2	1399.1
4 Herbicide and salvage log	43	63.6 ± 14.9	2.1	434.5	394.1	382.3	2198.6
1–4 Treated	176	50.4 ± 7.9	2.1	980.8	175.0	169.8	1579.4
5 Control	42	36.4 ± 5.4	5.8	191.1	69.0	66.9	736.2

Surface stormflow from these forested watersheds averaged 3% of the total rainfall. Only five storm events produced flow in excess of 10% gross rainfall (11—36%).

Although analysis of stormflow response from herbicide application was not an objective of this study, stormflow volumes for the 784-day period show some interesting trends. Total stormflow volume (3% of rainfall) for the hexazinone-treated watersheds (Table 1) was double that of the control. This agrees with results from other small forest watershed studies in the Piedmont. Douglass and Goodwin (1980) reported a twofold increase in runoff with minimum intensity mechanical site preparation over a 3-year period. They also measured storm runoff as 9% of total rainfall. In another study (Douglass and Van Lear, 1983), burning of understory vegetation did not affect stormflow volumes on forested watersheds with similar runoff (3—12% of precipitation). Thus, normal stormflow of these small watersheds can be doubled by eliminating forest transpirational use of water. Large stormflow increases (fourfold to eightfold), which produce adverse sediment and nutrient outputs, occur only where extensive soil disturbance occurs.

Herbicide residues

Movement of hexazinone residues in stormflow is discussed in detail by Neary et al. (1983). From 26 April 1979 until 21 May 1980, 26 storms were monitored to determine the stormflow concentrations and outputs of hexazinone and its two primary metabolites (Fig. 2). Residues in runoff peaked in the first storm after application (442 mg m^{-3}) and declined rapidly to around 100 mg m^{-3} by the second storm. Herbicide residues were still detectable in trace levels until 28 March 1980. Two metabolites occurred in runoff in low-to-trace concentrations (< 23 mg m^{-3}). Loss of hexazinone in stormflow averaged 0.53% of the applied herbicide, with two storms accounting for more than half of the loss. Concentrations of hexazinone in stormflow were never high enough to produce any phytotoxicity in aquatic macrophytes or algae (Fowler, 1977). An in situ study of aquatic invertebrates below the four treated watersheds determined that there were no herbicide-related impacts to species composition or diversity (Mayack et al., 1982).

Sediment

Sediment output from the four treated watersheds was almost entirely in the suspended phase. This was true even after the shortleaf pine and firewood salvage operations in early 1980. Only one storm, Storm 3, produced any coarse sediment deposition. Coarse sediment collected in the flumes averaged less than 0.4 kg per watershed.

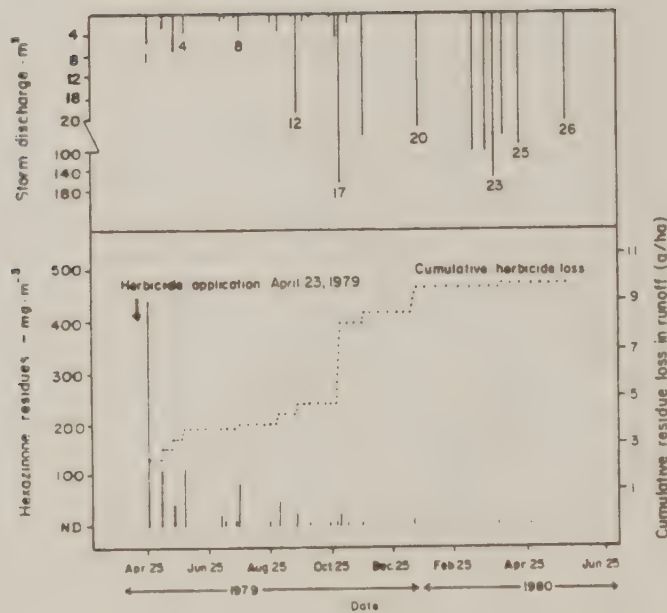Suspended solid concentrations were determined on flow-proportional

Fig. 2. Mean hexazinone residues (parent compound plus two metabolites) in storm runoff (vertical bars), cumulative output of residues (dots), and runoff volume (Storms 1—36), 23 April 1979 to 27 May 1980 (after Neary et al., 1983).

samples from 43 of 62 storm events (Fig. 3). This encompassed 99.7% of the total stormflow during the study. Mean suspended solids concentration on the four herbicide-treated watersheds (50.4 ± 7.9 g m^{-3}) (mean $\pm$ standard error) was slightly higher than that for the control watershed (36.4 ± 5.4 g m^{-3}) (Table 1). Concentrations ranged from a low of 2.1 g m^{-3} on herbicide treated and logged WS 4, to a high of 980.8 g m^{-3} on herbicide-treated but not logged WS 3.

There was no apparent relationship between logging and suspended sediment concentrations (Fig. 3). Soil disturbance on the logged watersheds was minimal ($<$ 14% bare soil). Felled trees were cable yarded to ridge access trails and skidders did not operate on side slopes or in the drainages. The highest suspended solids concentration (980.9 g m^{-3}) came from WS 3 which was hexazinone-treated but unlogged. Again, this indicates that without major soil disturbance normal channel characteristics and dynamics were the controlling factors in sediment concentrations. In five of the pre-logging storms, the control watershed had the highest suspended solids concentrations. Only two of the storms after logging produced higher values on the herbicided and logged watersheds.

Suspended sediment output ranged from a low of 69.0 kg ha^{-1} on the control WS 5 to a high of 394.1 kg ha^{-1} on WS 4. This latter watershed was the most steeply incised and had the longest channel length. Most of the sediment output (97%) occurred during the first 365 days of the study. Storms 34—62, occurring during the last 411 days, accounted for
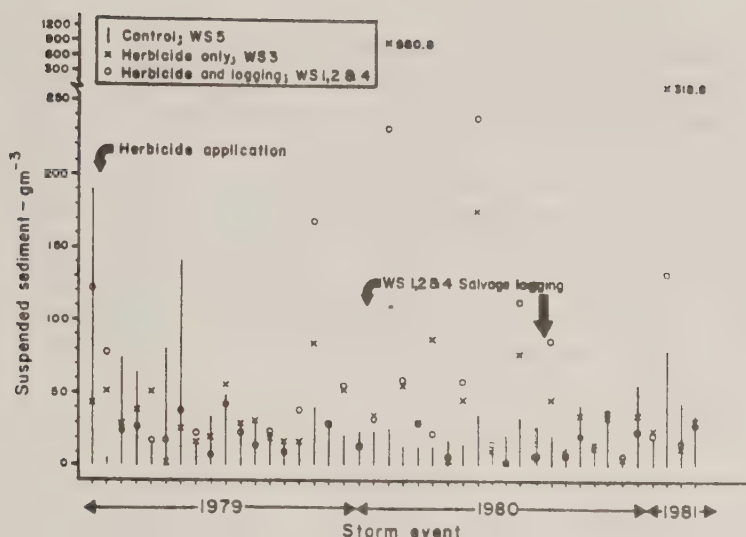
Fig. 3. Suspended solid concentrations in stormflow from the (1) hexazinone-treated, (2) hexazinone-treated and logged, and (3) control watershed, 16 April 1979 to 3 April 1981.

a relatively small proportion (< 13%) of the total stormflow volume, and hence sediment output.

Although the sediment outputs from the hexazinone-treated watersheds were 2.5 times that of the control, this difference was a very small rise above background sediment delivery rates. Most of this increased output was due to higher stormflow volumes from the herbicide watersheds (Table 1). Elimination of transpiring vegetation and exposing of the ephemeral channels to direct raindrop impact doubled the stormflow. Looking at stormflow volume-adjusted sediment outputs, the control produced 0.091 kg m^{-3} during the study. The hexazinone-treated watersheds were only slightly higher with 0.108 kg m^{-3}. Among these four watersheds, WS 1, 2, and 3 produced 0.066, 0.077, and 0.075 kg m^{-3}. Watershed 4, with steeper topography and incised channel, had a higher sediment output of 0.174 kg m^{-3}.

Application of hexazinone eliminated transpiration use of rainfall but did not reduce soil infiltration capacity. Since careful logging kept soil disturbance to < 14%, sediment sources were not available to produce large outputs. The presence of leaf litter during the first year and extensive ground cover during the second mitigated any adverse effects of vegetation removal on sediment yields. Data reported elsewhere in the southern United States indicate that sediment yields from undisturbed forest watersheds are generally less than 100 kg ha^{-1} year^{-1}. Exceptions do occur, particularly on loess soils such as those reported by Beasley (1979) where natural sediment production is 600—700 kg ha^{-1} year^{-1}. Compared to other site preparation practices, herbicide control of competing vegetation does not

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adversely affect sediment yields or water quality. Sediment yields from burning are somewhat lower, at 44 kg ha⁻¹ (Douglass and Van Lear, 1983), but those from mechanical site preparation are significantly higher at 12000—15000 kg ha⁻¹ (Douglass and Goodwin, 1980).

Sediment losses in streamflow after mechanical site preparation do decline after the first year. However, during the first year they approach losses found in agricultural ecosystems (8000—13000 kg ha⁻¹ year⁻¹). These sediment losses represent the greatest disturbance to both site productivity and water quality. Thus, use of chemicals like hexazinone in site preparation could significantly reduce a major adverse environmental impact produced during harvesting and reforestation.

Nitrate nitrogen

Concentrations of NO₃-N in stormflow became distinctly elevated above those of the control watershed beginning in July, about 80 days after the hexazinone application (Fig. 4). The peak pulse of NO₃-N occurred in October 1979, with a concentration of 5328 mg m⁻³. During the winter months, NO₃-N levels dropped to within range of the control, but then rose again in the spring (peak of 2530 ± 254 mg m⁻³). These peak concentrations exceeded those measured for other types of forest site disturbance in the region by one to two orders of magnitude (Swank and Douglass, 1977; Huff et al., 1978; Hewlett, 1979; Vitousek and Mellilo, 1979; Swank and Caskey, 1982; Douglass and Van Lear, 1983). However, the peak concentration never exceeded the water quality standard and persisted for only 2 years. The pulsing of NO₃-N, followed by a recovery and secondary pulse
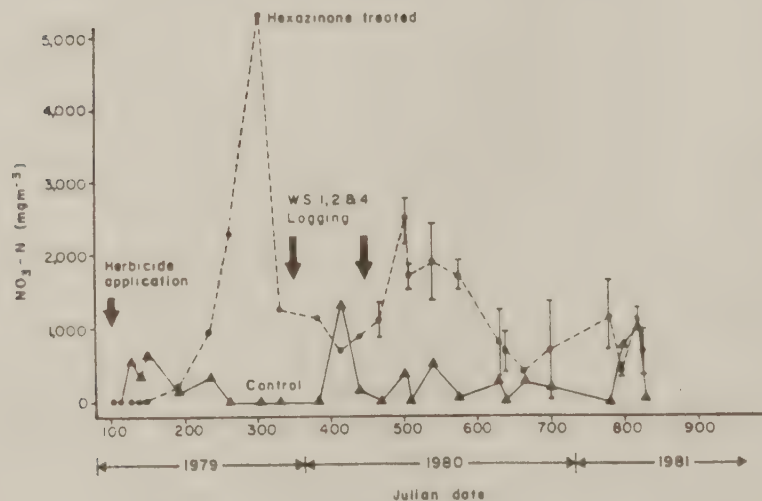

Fig. 4. NO₃-N concentrations (± standard errors) in storm runoff from hexazinone-treated and control watersheds, 16 April 1979 to 3 April 1981.

the next year, follows a pattern of ecosystem response to disturbance with gradual recovery to equilibrium. The response of NO_3-N to hexazinone application also is reminiscent of that observed at Hubbard Brook, NH, where a herbicide was used to suppress a northern hardwood forest (Likens et al., 1970). However, the magnitude of NO_3-N increase was one-half that observed at Hubbard Brook. Similar NO_3-N losses in response to herbicides used during site preparation in the Piedmont have been reported by Vitousek and Matson (1984).

The increased NO_3-N release from this forest ecosystem can be partially explained by the termination of nitrate uptake during the warm summer months with the killing of most of the dominant vegetation. Very little understory remained after the hexazinone application to respond to the sudden removal of the canopy (Neary et al., 1981). Understory woody and herbaceous plants responded rapidly the second growing season to occupy the site. This would explain decreased NO_3-N concentrations in the second summer.

Another explanation for increased NO_3-N in stormflow from the hexazinone-treated watersheds is that microbial populations, which influence nitrogen cycling, were affected. Two key microbial populations involved in the nitrogen cycle are denitrifiers and nitrifiers. If denitrification were inhibited, the conversion of nitrate (NO_3^-) to N_2-O and N_2 would be retarded, thus increasing the concentration of NO_3-N in hexazinone-treated soils. Alternatively, stimulation of the two-step nitrification process might increase the oxidation of ammonia (NH_4) to nitrite (NO_2^-) and NO_2^- to NO_3^-. Increased soil moisture and soil temperature are known to stimulate nitrifier activity in disturbed forest ecosystems (Vitousek and Mellilo, 1979).

Another hypothesis relating to moisture and temperature stimulation of nitrifiers is that of direct stimulation by hexazinone. Other triazine herbicides like atrazine and simazine have been shown to stimulate soil microflora including nitrifiers (Percich and Lockwood, 1978). Since hexazinone is in the same group of herbicides, it could also be stimulating nitrifiers and hence increasing NO_3-N abundance in the watershed system.

Vitousek and Matson (1984) have suggested a fourth hypothesis. They conclude that disturbance of the forest floor through shearing, piling, and discing removes a major nitrogen sink-microbial immobilization. In this study, the forest floor was undisturbed the first year and no biomass removal occurred. Thus, this hypothesis was not considered to be of major importance.

A study was conducted to test the third of these hypotheses. At concentrations of 10 and 100 mg kg^{-1}, hexazinone had no apparent effect on denitrifiers. Nitrous oxide production by mixed denitrifier populations in soil slurries was not significantly different in control or hexazinone-treated cultures. After a 72-h incubation, the quantity of nitrous oxide production was 2591, 2501, and 2519 nmol for cultures with 0. 10, and

100 mg kg^{-1} of hexazinone, respectively. Similarly, nitrous oxide and carbon dioxide production by pure cultures of *Pseudomonas fluorescens* were not significantly different in control or hexazinone-treated flasks. Finally, periodic determination of number of denitrifiers in soil samples collected between June 1980 and February 1981 revealed no significant difference between population levels in soil from control and hexazinone-treated watersheds.

At concentrations of 10 and 100 mg kg^{-1}, hexazinone had no significant effect on the nitrifier *Nitrosomonas europaea*. After 5 days incubation, the total number of cells in a control culture was 9.7×10^7 ml^{-1}, while te final numbers in the presence of 10 and 100 mg kg^{-1} were 9.62×10^7 ml^{-1} and 1.0×10^8 ml^{-1}, respectively. Similarly, production of NO$_2^-$ by these cultures was not significantly different. However, hexazinone stimulated the nitrifier *Nitrobacter winogradskyi*. Concentrations of 10 and 100 mg kg^{-1} stimulated growth and NO$_2^-$ oxidation by this species to approximately the same extent (Fig. 5).
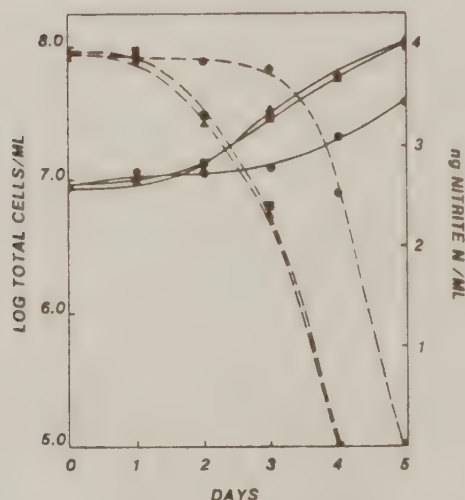

Fig. 5. Effects of hexazinone on growth and nitrate utilization by *Nitrobacter winogradskyi* (●——●) Total cells, control culture; (■——■) total cells, culture amended with 10 ppm hexazinone; (▲——▲) total cells, culture amended with 100 ppm hexazinone. Symbols are the same for nitrite values but are connected by dashed lines.

The results imply that hexazinone had little inhibitory effect on denitrification. This corresponds to a number of reports which indicate that the denitrifying population of most soils is not readily susceptible to inhibition by pesticides (Wainwright, 1978). However, the results support the possibility that hexazinone stimulates the overall process of nitrification. The first step in the process, oxidation of NH$_4^+$ to NO$_2^-$ does not appear to be affected, assuming that *Nitrosomonas europaea* typifies the response of in situ ammonia oxidizers. Reports indicate *Nitrosomonas europaea*

is, in fact, an important species in this first step of nitrification (Schmidt, 1978). Stimulation of *Nitrobacter winogradskyi* indicates that the second step in nitrification, oxidation of NO_2^- to NO_3^-, might be enhanced in the presence of hexazinone. Hexazinone is structurally related to atrazine, and stimulation of pure cultures of *Nitrobacter winogradskyi* by the addition of 250 g m^{-3} atrazine has been measured. Rhodes et al. (1980) measured total NO_3^- formation in soil-filled containers amended with hexazinone. They did not detect increased NO_3^- production and conclude that nitrification was not being affected. The soil in their experiment was amended with NH_3, which is the energy source for nitrifiers such as *Nitrosomonas europaea*. These bacteria are not affected by hexazinone according to our results.

Anions/cations

The anion and cation contents of storm runoff from the herbicide-treated and control watersheds were quite variable (Table 2). Mean concentrations of NO_3-N, K^+, and Mg^{2+} were significantly higher in stormflow from the hexazinone-treated watersheds. Calcium concentrations were also increased, but not significantly so. Chloride concentrations were significantly higher on the control watersheds rather than the herbicide treated ones. Magnesium concentrations nearly doubled as a result of the hexazinone treatment. Both potassium and Ca^{2+} concentrations increased by 30%. Since anion and cation flux through soil and watershed systems is generally in mass balance, the increased release of anions from the soil must result in higher

TABLE 2

Mean concentrations of anions and cations in storm runoff from four hexazinone-treated and one control watershed in the upper Piedmont, 1979—1981

Parameter	Mean concentration ± S.E.		
	Hexazinone treated (pH = 5.72 ± 0.04) (mg m^{-3})	Control (pH = 5.97 ± 0.08) (mg m^{-3})	Significance[a] NS
Nitrate nitrogen	1147 ± 120	280 ± 69	***
Ammonia nitrogen	281 ± 42	392 ± 84	NS
Orthophosphate	164 ± 27	264 ± 61	NS
Chloride	1443 ± 54	1652 ± 161	**
Potassium	3168 ± 250	2541 ± 331	*
Sodium	615 ± 33	697 ± 85	NS
Calcium	1309 ± 66	1013 ± 104	NS
Magnesium	922 ± 46	548 ± 46	***
Sulfate	6406 ± 176	7198 ± 451	NS

[a]t-test significance: $P < 0.001$ = ***; $0.001 < P < 0.01$ = **; $0.01 < P < 0.05$ = *; NS = nonsignificant.

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loss of cations. Thus, the higher concentrations of K$^+$, CA^{2+}, and Mg^{2+} are consistent considering the larger amounts of negatively-charged nitrate moving through the system (Table 2).

The pattern of cation increased (i.e., Mg) was identical to that of the NO$_3$-N anion (Fig. 6). As with NO$_3$-N, the initial increases did not persist and returned close to levels of the control within 2 years. The main treatment effect occurred with the herbicide application. Removal of scattered shortleaf pine and already dead hardwoods did not produce any significant effect in 1980 (Fig. 6). The rise in cation concentrations the summer after logging (1980) reflected ecosystem resilience in returning to cation baseline concentrations (Swank and Waide, 1980). The perturbation to anion and cation concentration equilibrium in stormflow was observed across all four herbicide-treated watersheds in 1979 and 1980. By 1981 the nutrient cycling mechanism was mainly restored due to extensive herbaceous ground cover (Figs. 4 and 6).

Although significant increases in cation concentrations occurred, they were within the range of variations for various forested watersheds in the region (Hewlett, 1979; Douglass and Van Lear, 1983). Also, the duration of the response was short due to the minimal soil disturbance and quick herbaceous vegetation recovery.
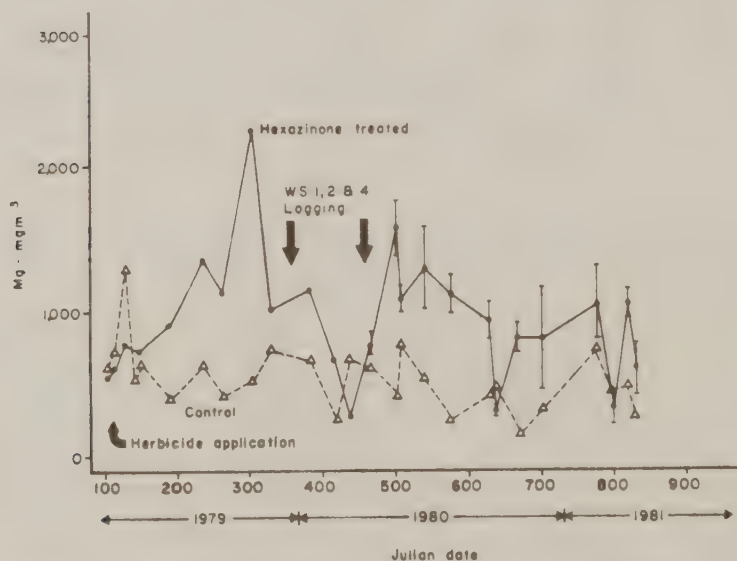

Fig. 6. Magnesium concentrations (± standard errors) in storm runoff from hexazinone-treated and control watersheds, 16 April 1979 to 3 April 1981.

Outputs

Outputs of anions and cations during the first year of the study — which accounted for 97% of the total stormflow — showed some considerable

treatment effects (Table 3). The combination of higher stormflow volumes and generally higher concentrations produced larger nutrient exports in the treated watersheds. This is even the case where mean ionic concentrations decreased as a result of hexazinone application. Some nutrient losses were higher than reported in other studies in the region (Douglass and Van Lear, 1983; Riekerk, 1982). However, losses of important nutrients like NO_3-N were less than observed at Hubbard Brook and Coweeta (Vitousek and Mellilo, 1979). Except for K, all losses from the herbicide-treated watersheds did not exceed normal inputs in rainfall. Part of this difference is due to the perennial streamflow at the latter two sites. Since only ephemeral storm-flow occurred in these watersheds, annual flow volumes were much smaller.

TABLE 3

Outputs of NO_3-N, NH_4-N, PO_4^{3-}, Cl^-, K^+, Na^+, Ca^{2+}, Mg^{2+}, and SO_4^{2-} in storm runoff during the first year after herbicide application to mixed hardwoods pine watersheds in the upper Piedmont

Parameter	Rainfall input (kg ha^{-1})	Nutrient output	
		Hexazinone treated[a] (kg ha^{-1})	Control[b] (kg ha^{-1})
NO_3-N	5.07	4.91	0.05
NH_4-N	2.40	0.82	0.03
PO_4^{3-}	0.50	0.34	0.04
Cl^-	16.69	6.60	0.89
K^+	3.37	12.88	1.26
Na^+	4.07	3.36	0.29
Ca^{2+}	4.11	5.98	0.55
Mg^{2+}	1.39	4.17	0.50
SO_4^{2-}	44.68	43.00	4.50

[a]Watershed 1, 2, 3, and 4.
[b]Watershed 5.

Increased nutrient losses were short in duration and generally did not exceed atmospheric inputs to the ecosystem. Thus, significant effects on site productivity or downstream water quality did not occur. Also, the measured losses into forest streams were much less than those resulting from agricultural activities.

SUMMARY AND CONCLUSIONS

Use of the herbicide hexazinone for controlling hardwood and herbaceous weeds prior to establishing pine stands should have no adverse affect on surface water quality. Data from this study indicate that chemical weed control using hexazinone is advantageous in that it produces much smaller water quality changes than commonly-used, intensive mechanical techniques.

Hexazinone was present in storm runoff for a period of 7 months, but concentrations were low. Losses of herbicide residue amounted to only 0.53%. Mean suspended sediment concentrations were elevated only slightly above those of the undisturbed control. Sediment delivery in stormflow was within the range of undisturbed forest watersheds of the region and far below that caused by intensive mechanical site preparation. Concentrations of some ions, particularly NO_3-N, were increased as a result of the herbicide treatment. However, these changes disappeared within 2 years, and outputs were within ranges observed in other disturbed forest watersheds.

The impacts on water quality produced by site preparation with hexazinone were small. When site preparation is necessary on steep slopes with fragile soils, application of herbicides should be a favored technique. This would prevent increased erosion and deterioration of water quality. Reforestation of eroded sites in the past 60—70 years has vastly improved water quality. The technology now exists for these stands to be harvested and the site regenerated without producing deterioration in water quality.

This publication reports research involving herbicides. All herbicides must be registered by appropriate state and federal agencies before they can be used. *Caution*: herbicides can be injurious to humans, domestic animals, desirable plants, fish or other wildlife if they are not handled or applied properly. Use all herbicides selectively and carefully. Follow recommended practices for the disposal of surplus herbicides and herbicide containers.

ACKNOWLEDGMENT

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